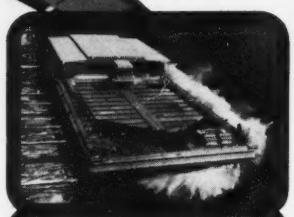
# Corrosion

Official Publication
NATIONAL ASSOCIATION OF CORROSION ENGINEERS

VOL. 14 SEPTEMBER, 1958 NO. 9

# The new corrosion film everyone is talking about!

Here is an authoritative film that answers many questions on the theory of corrosion and demonstrates methods by which it is controlled. Presented in color and sound, it ranges from the formation of anodes and cathodes through the use of galvanizing, inhibitors, metallizing, cathodic protection, alloys and protective coatings. You will see how many corrosion problems in industries such as yours are being solved by Dimetcote, a one-coat zinc silicate protective coating. This film will be well worth 19 minutes of your time. To arrange a showing for you and your associates, or to learn when it will be shown in your area, contact any of the Amercoat offices listed below.



**Typical audience reactions:**

Bishop, Tex.—"Planning fair-sized test after seeing this film."

Louisville, Ky.—"Answers many questions. Second showing arranged."

Cincinnati, Ohio—"Key personnel evidenced considerable interest."

Netherlands Antilles—"Both shows led to 45-minute discussions."

Fairport, Ohio—"Very interesting. Will try methods shown."

Las Piedras, Venezuela—"Putting ideas to work in near future."

Bartlesville, Okla.—"Viewed by 42 key men from five divisions."

**Answers these and other questions:**

What produces electrolytic corrosion?

What factors favor hot-dip galvanizing?

How important is surface preparation?

Can a coating survive a tank fire?

Can rust in tankers be controlled?

Can a coating offer cathodic protection?

What are the corrosion problems on offshore rigs?

What are the advantages of zinc silicate?

How can chemical plants cut painting costs?

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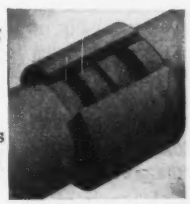

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# CONTENTS

Corrosion

devoted entirely to corrosion research and control

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Vol. 14 September, 1958 No. 9

Page

This Month's Cover ..... 4

Directory of Regional and Sectional Officers ..... 6, 8, 10

Officers and Directors, Staff Members, National Association of Corrosion Engineers ..... 20

## TECHNICAL COMMITTEE ACTIVITIES

Water Industry Corrosion Problems Discussed ..... 65

Increasing Damage From De-Icing Salts Feared ..... 65

Static Inhibitor Test Completion Urged by T-1K ..... 65

Sea Water Silt Tests Planned for Anodes 65

Tape Committee Holds Sessions At Three Regional Meetings ..... 66

Long Range Evaluation of Plastics Planned 66

Rectifier Ripple Inquiry on Agenda ..... 66

New Questionnaire Given to Cable Sheath Group ..... 66

Discussion of Zero Resistance Ammeter Held by Group TO4B-3 ..... 68

More AC Corrosion Reports Given ..... 68

Copying of Coordinating Committee Maps Weighed ..... 68

HF Alkylation Query Data Are Summarized ..... 68

Stray Current Inquiry ..... 68

Redox Interpretation Is Topic ..... 68

## NACE NEWS

### SOUTH CENTRAL REGION CONFERENCE

New Orleans Meeting Plans Completed .. 69

Schedule of Technical Meetings ..... 69

South Central Region Abstracts ..... 69

South Central Region Conference Authors and Officials ..... 70

• • •

Mailings Planned for Western Region's Nov. 17-21 Meeting ..... 74

(Continued on Page 4)

## TECHNICAL SECTION

Page

**Topic of the Month—Corrosion of Titanium in Sulfuric Acid and Chlorine**
*By L. W. Gleekman* ..... 21

**A Review of the Gas Condensate Well Corrosion Problem**
*By D. R. Fincher* ..... 23

**Corrosion Resistance of Titanium Alloys Compared With Commercially Pure Titanium**
*By David Schlain and Charles B. Kenahan* ..... 25

**Effect of the Concentration of Various Salts On the Dissolution of Cadmium in Air Saturated Solutions**
*By Charles J. Boone and Cecil C. Lynch* ..... 29

**Saturable Reactors for Control Rectifiers**
*By Harry E. Kroon* ..... 32

**SYMPOSIUM ON CORROSION BY HIGH PURITY WATER**

Four Contributions to the Work of NACE Technical Committee T-3F on High Purity Water. Publication 58-13.

**The Corrosion Behavior of Zirconium-Uranium Alloys in High-Temperature Water**
*By Warren E. Berry and Robert S. Peoples* ..... 34

**Corrosion and Water Purity Control for the Army Package Power Reactor**
*By Richard J. Clark and A. Louis Medin* ..... 39

**Removal of Corrosion Products from High Temperature, High Purity Water Systems With an Axial Bed Filter**
*By R. E. Larson and S. L. Williams* ..... 44

**Some Relations Between Deposition and Corrosion Contamination in Low Make-Up Systems For Steam Power Plants**
*By E. S. Johnson and H. Kehmna* ..... 49
Discussion: Robert D. Misch, Page 53; B. A. Kronmiller, Page 53; W. A. Keilbaugh, Pages 53 and 54; Replies by E. S. Johnson and H. Kehmna, Page 54

**Corrosion of Metals in Tropical Environments (Part 2—Atmospheric Corrosion of Ten Structural Steels)**
*By C. R. Southwell, B. W. Forgeson and A. L. Alexander* .... 55

**A Method for Determining Corrosion Rates From Linear Polarization Data**
*By Milton Stern* ..... 60

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# CONTENTS

(Continued From Page 3)

## NACE News


| | Page |
|---|---|
| NORTH CENTRAL REGION MEETING | |
| Outstanding Program Arranged for Cincinnati October 15-17 | 76 |
| Technical Program Chairmen and Authors | 77 |
| North Central Region Abstracts | 78 |
| North Central Region Biographies | 82 |
| • • • | |
| National and Regional Meetings and Short Courses | 85 |
| Teche Section Meeting | 85 |
| Miami Corrosion Control Short Course Set Nov. 10-14 | 85 |
| 12 Papers Arranged for Richmond Meeting | 86 |
| Men Responsible for Western Region Conference and Corrosion Control Short Course | 86 |
| Poor Coating Job Doubles Cost in 5 Years | 88 |
| Canadian Region Sets Double Meetings | 90 |
| Everything Is Ready for San Joaquin Tour | 90 |
| Deep Ground Beds Is Topic at Birmingham | 90 |
| Burnett Will Be Chairman of Denver Regional Meeting | 90 |
| Technical Program for 1960 Northeast Meeting Outlined | 90 |
| Kansas City Section to Chart Activities for 1959 | 90 |
| Waldrip Speaks at Calgary | 90 |
| Saleck to Run Short Course | 90 |
| • • • | |
| NORTHEAST REGION MEETING | |
| Well-Balanced Program Is Completed | 92 |
| Registration Times, Fee Schedule | 92 |
| Naval Shipyard and Clapp Laboratory Tours Arranged | 92 |
| Variety of Entertainment Includes Ladies' Program | 92 |
| Four Industrial Films to Be Shown | 92 |
| Old-Fashioned Clam Bake Entertainment Highlight | 94 |
| • • • | |
| Logan Joins Committee | 92 |


## General News


| | |
|---|---|
| Corrosion Course Is Offered at Houston University | 95 |
| Louisville Industries Are Charged With 85% of Air Pollution Load | 95 |
| Coatings School Set September 6 and 13 | 95 |
| Quick Identification by Crystal Facial Angels Is Facilitated by Catalog | 95 |
| Papers on Environmental Testing, Simulation Sought | 95 |
| ASTM Atmospheric Testing Results Given at Boston Meeting | 95 |
| Magnetic Ball Check Valve Uses No Springs | 96 |
| Mathematics, Physical Sciences Course Offered | 96 |
| St. Mary's Offers BS | 98 |
| Book News | 100 |
| New Products | 102 |
| Men in the News | 104 |


## Technical Topics


Some Corrosion Problems of Tank Trucks and Their Solutions *By Louis Reznek* ..... 105

INDEX TO CORROSION ABSTRACTS ..... 113

INDEX TO ADVERTISERS ..... 128


**SCHEDULED FOR PUBLICATION IN OCTOBER TECHNICAL TOPICS**

More Revenues from Longer Lasting Water Meters Through Corrosion Control by *Harold E. Wilson*

Tests Show Most Coatings Blister Under Cathodic Protection by *F. J. Ploederl*


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**THIS MONTH'S COVER—Shown here are some of the 7000 boxcars operated by Canadian National Railways with unpainted aluminum roofs. CNR adopted the roofs as standard in 1955. Alloy is Alcan B54S (nominal 4.4 Mg 0.30 Mn) 0.081 thick riveted with Alcan 55S rivets. (Cu-free balanced $Mg_2Si$ alloy).**

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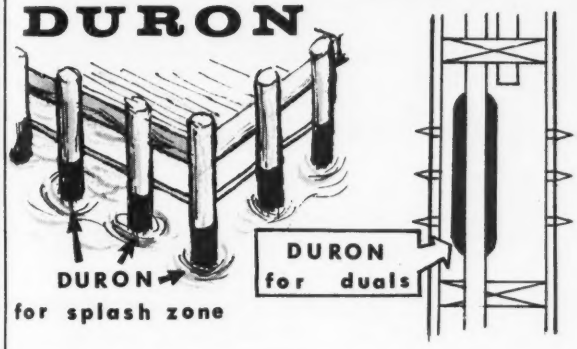


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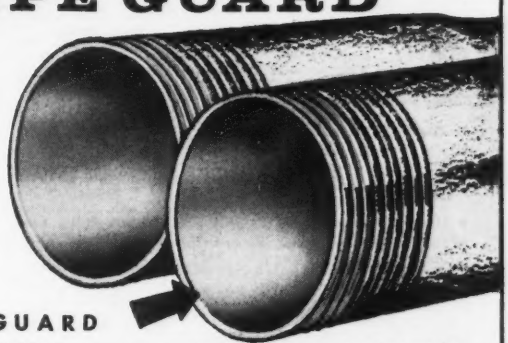


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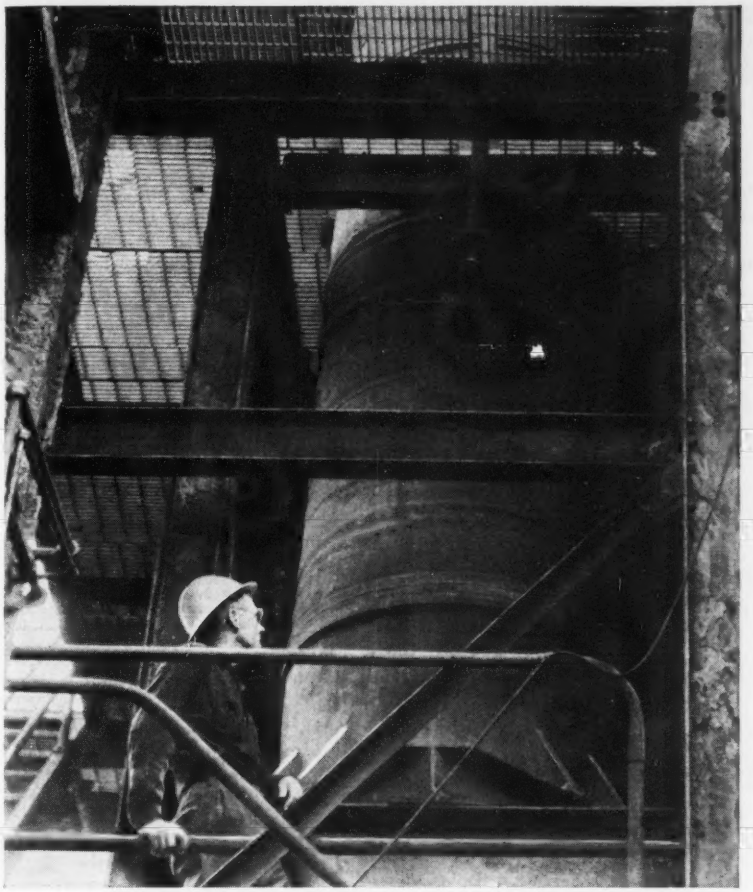
(Continued on Page 8)



## Results of 133-day Plant Corrosion Tests in Distillation and Rectification of Crude $CCl_4$

### TEST 1

Suspended in vapor stream above top plate of bubble cap rectification column. Approximate analysis of vapor:

| | |
|---|---|
| Carbon Tetrachloride | 99.398% |
| Sulfur Chloride | 0.600% |
| Carbon Bisulfide | 0.002% |

Temperature: 78°C. (171°F.)

### TEST 2

Suspended in reboiler for column, completely immersed in liquid with following approximate analysis:

| | |
|---|---|
| Sulfur Chloride | 98.30% |
| Carbon Tetrachloride | 0.13% |
| Iron as $FeCl_3$ | 0.01% |

Temperature: 138°C. (280°F.)

**CORROSION RATE**

| | TEST 1 ipy.** | TEST 2 ipy. |
|---|---|---|
| Monel | † | † |
| Nickel | † | † |
| Inconel | † | † |
| Ni-Resist (Type 5) | † | 0.001 |
| Ni-Resist (Type 1) | † | 0.002 |
| Mild Steel | 0.008 | 0.217 |
| Cast Iron | 0.007 | 0.128 |

**inches penetration per year †less than 0.001

# Maintenance cost cut 90% in $CCl_4$ system

*Using 3 different Nickel alloys, Westvaco runs column and reboiler 12 years. Savings exceed $108,000*

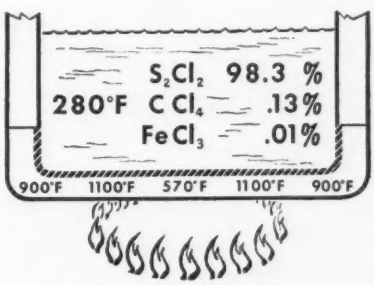
At Westvaco Chlor-Alkali Division of Food Machinery and Chemical Corp., corrosion by sulfur chloride had been causing failure of the bottom head of the reboiler in the $CCl_4$ system every 15 months. Other parts, too, had to be replaced frequently . . . running maintenance costs up to $10,000 per year and more.

Engineers tested various materials in critical environments in the system. The data showed that several nickel alloys provided superior corrosion resistance. And the system was redesigned using these alloys. In the 12 years since, there have been no replacements of major units. Yearly maintenance has stayed below $1000.

### Reboiler bottom head

This item, originally cast iron, is now 10% Inconel-clad steel made by Lukens Steel Co. with fire-box steel backing.

The Inconel* nickel-chromium alloy has high resistance to chlorinated organic solvents and also resists sulfidation at the high temperatures present. Sketch shows conditions.




### Vapor, return and drop lines

These lines are all Monel* nickel-copper alloy.

Monel alloy provides protection against the small amounts of dilute hydrochloric acid likely to form by hydrolysis in these cool parts of the system.

Ni-Resist* high nickel cast iron completed the redesign. It was used for sides and top of the reboiler and for bubble caps, trays, and bottom sections of the still shell, which had originally been designed for cast construction.

### Is your maintenance cost too high?

Is corrosion or high temperature the likely cause? Inco's Development and Research Section can help you pin down the facts and select corrective alloys.

*Registered trademark

**The International Nickel Company, Inc.**
67 Wall Street New York 5, N.Y.

INCO NICKEL ALLOYS

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(Continued From Page 6)

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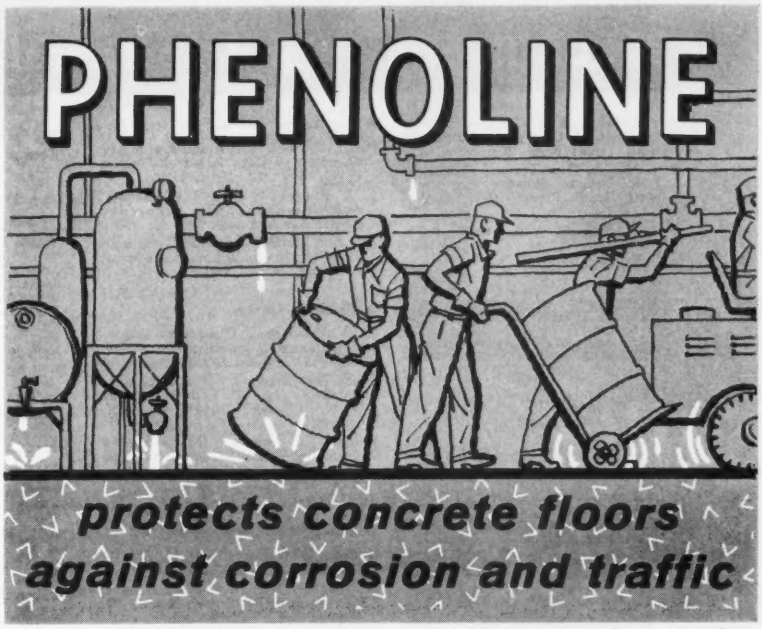
(Continued on Page 10)

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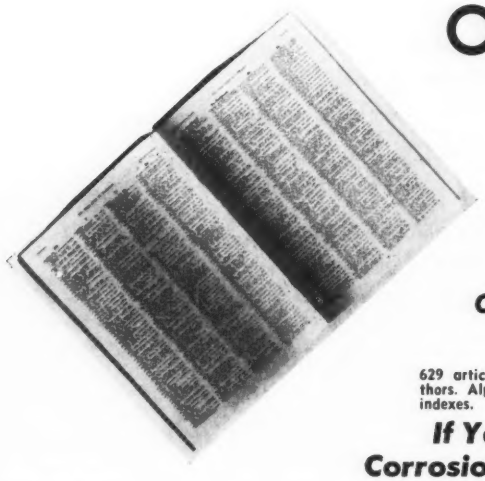

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# In Coatings, Watch Epoxy

**New types of protective materials for prevention of external pipe corrosion—as well as new additions to old types—are vying for the attention of pipeline builders.**

Electrolytic corrosion, caused by currents emitted from pipe metal, is the chief enemy of engineers fighting external pipe corrosion. This corrosion can be counteracted by halting the outflow of electricity. But there's only one way to do that—by enclosing the pipe in a material that will not leave even minute parts of the pipe exposed, regardless of time and soil conditions.

Although the protective coverings developed for pipe to date have many important advantages, no one has come up with the perfect material—the one that will eliminate such corrosion completely. (The "perfect material" would differ according to the conditions of each line.)

Perhaps no one will ever come up with the perfect covering, but manufacturers are trying.

**Epoxy resin coatings are attracting a good deal of interest as external-corrosion preventives.**

Epoxy resin coatings are made from petroleum-derived materials. They're said to combine into one package many of the individual advantages of other coatings.

One industry representative whose job it is to keep tabs on coating developments recently told PETROLEUM WEEK, "Within the next year or two, there will be marked improvement in epoxy resins [coatings], which could enable them to replace some present hot-enamel-type coatings."

Coast Paint & Lacquer Co. came out with one late last year (PW—Dec.20'57,p46). The coating, applied hot, is said to be especially fast-drying.

Coast is one of the 11 associated companies called Copon Associates. The other companies, spread around the country, are now either already marketing, or getting ready to market, the epoxy coating Coast developed last year.

Pittsburgh Coke & Chemical Co., which has marketed a cold-applied similar coating, "Tarset," for other industrial uses for a few years, is now making it available for pipeline application.

Pitt Chem's entry into the field of cold-applied epoxy resin pipeline coatings must certainly be taken as a sign of the times, because the company has for years been marketing a hot enamel coating. Now "Tarset" is moving into direct competition with the older Pitt Chem coating product.

"Tarset," a coal tar epoxy resin which provides protection in a temperature range from —30F to 400F, was recently applied on one system in Venezuela and is now ready for the U. S. market.

Other companies are known to be in experimental stages with similar epoxy type coatings.

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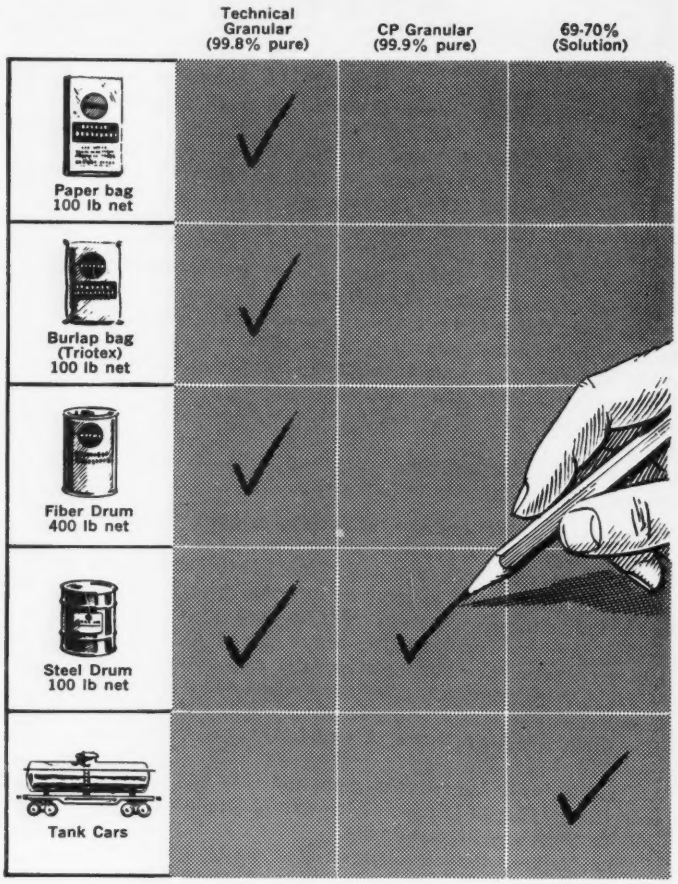
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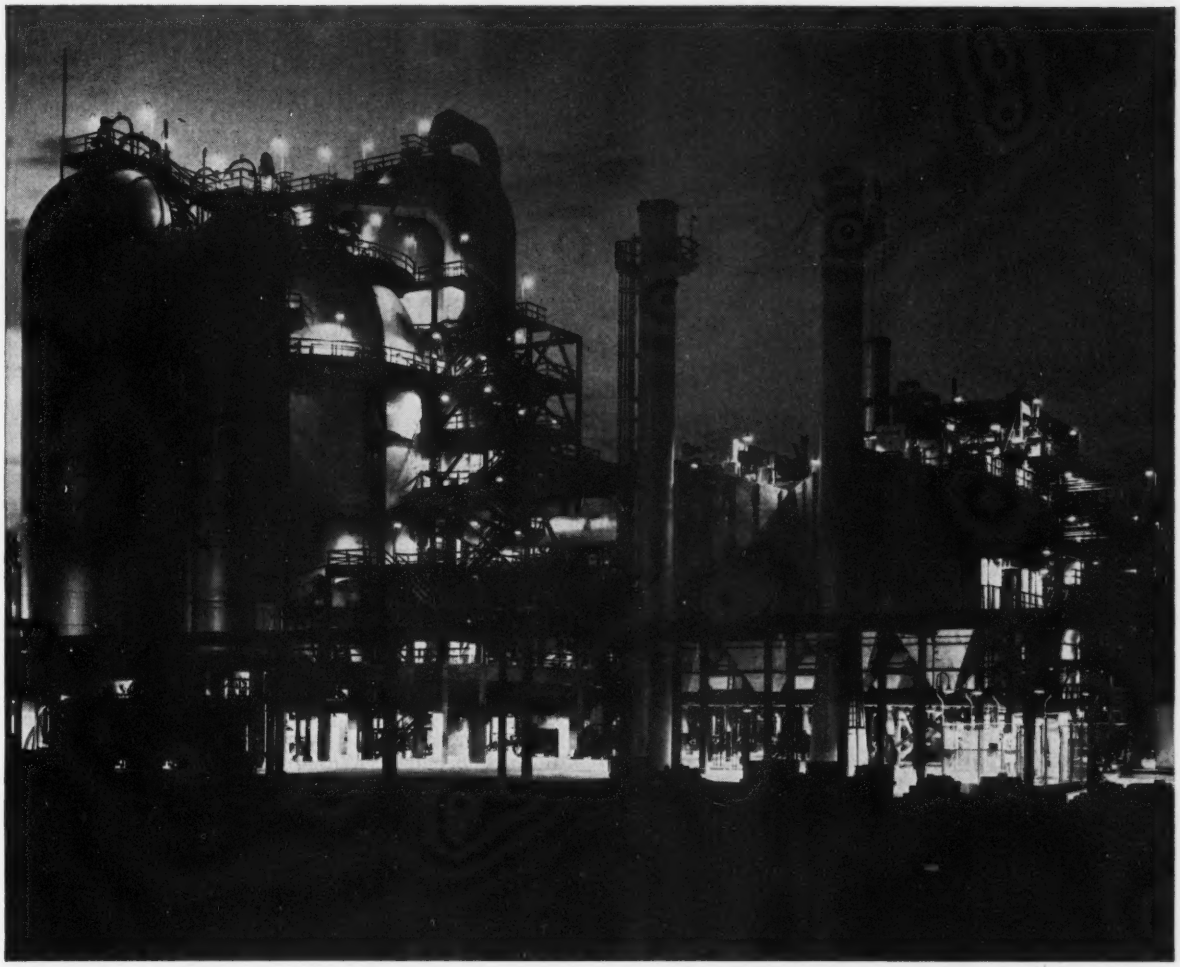

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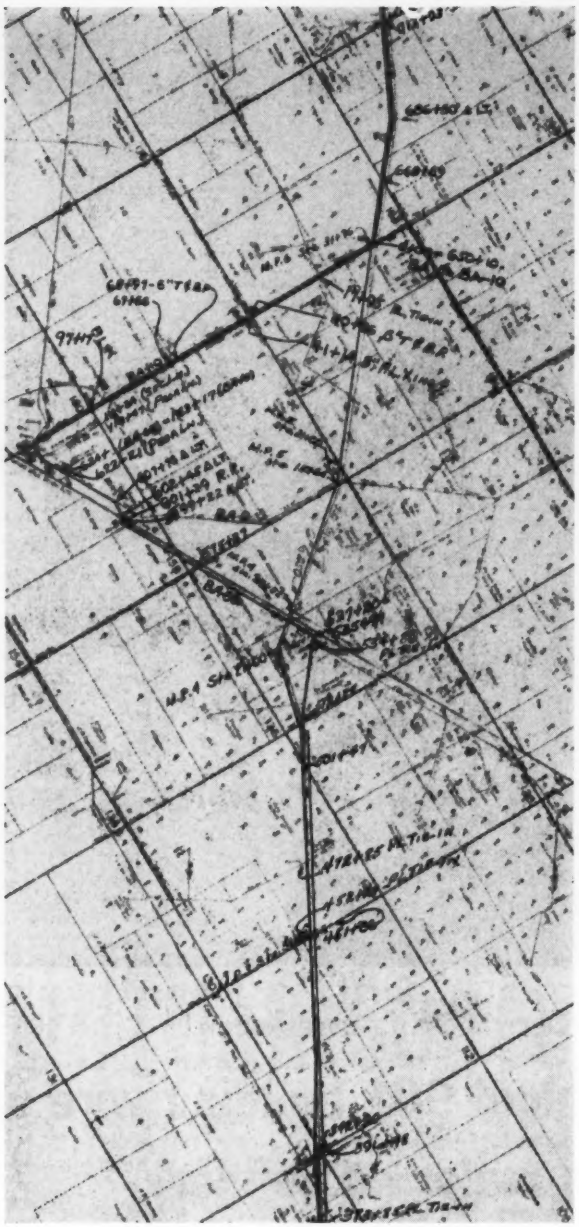

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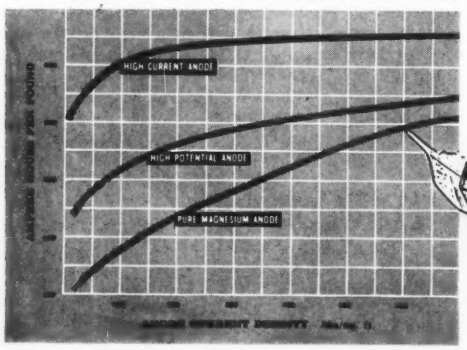


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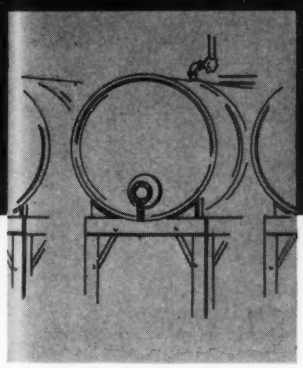

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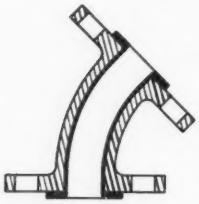

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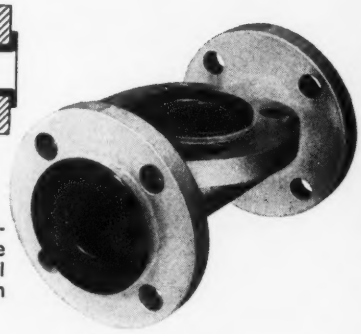

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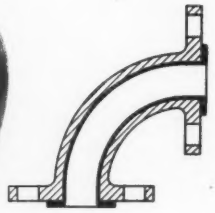

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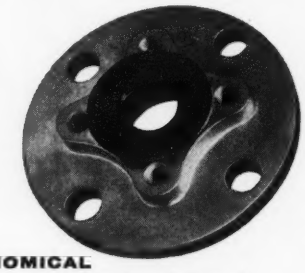

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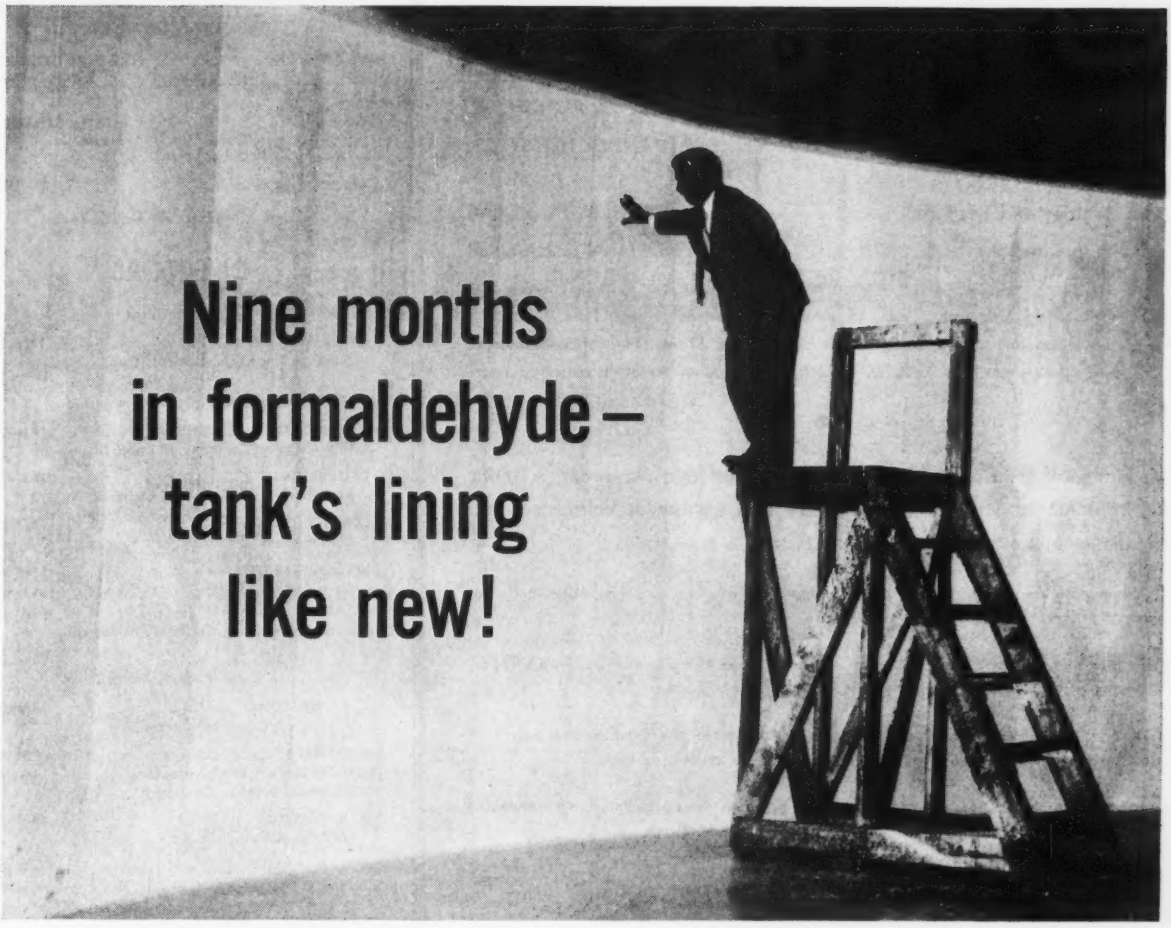


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(a) To promote the prevention of corrosion, thereby curtailing economic waste and conserving natural resources.

(b) To provide forums and media through which experiences with corrosion and its prevention may be reported, discussed and published for the common good.

(c) To encourage special study and research to determine the fundamental causes of corrosion, and to develop new or improved techniques for its prevention.

(d) To correlate study and research on corrosion problems among technical associations to reduce duplication and increase efficiency.

(e) To promote standardization of terminology, techniques, equipment and design in corrosion control.

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(g) To foster cooperation between individual operators of metallic plant and structures in the joint solution of common corrosion problems.

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Corrosion

OFFICIAL MONTHLY PUBLICATION

National Association of Corrosion Engineers

An Association of Individuals and Organizations Concerned with Control of Corrosion

1061 M & M Building Houston 2, Texas

Vol. 14 September, 1958 No. 9

Topic of the Month

# Corrosion of Titanium In Sulfuric Acid and Chlorine

By L. W. GLEEKMAN*

## Introduction

A SERIES of laboratory and plant tests were conducted recently to find suitable materials of construction to handle both chlorine gas being dried by sulfuric acid and sulfuric acid saturated with chlorine. In these tests, 50 percent sulfuric acid and 87 percent sulfuric acid were used inasmuch as they corresponded to particular plant conditions in the drying of chlorine.

The corrosion data in Figure 1 show the results of a laboratory test in which commercially pure titanium A-70 was tested in 50 percent sulfuric acid saturated with chlorine-air mixtures. Samples of commercially pure titanium A-70 were immersed in wide mouth bottles which held the sulfuric acid. One sample totally was immersed in the acid, one sample partially immersed and one sample exposed in the vapor phase.

Mixtures of chlorine and air were introduced into the sulfuric acid with a diffuser which bubbled the gaseous mixture through the acid. The gaseous mixture ranged from 100 percent air to 100 percent chlorine with particular interest being directed to the high chlorine and the high air percentages. The gaseous composition was determined by a modified Orsat apparatus with pressure regulators and flowmeters being located on the chlorine and air sources. The gaseous mixture was added to the acid solution for eight hours continuously during the day; the bottles were then closed off to the atmosphere over night. The test ran for two weeks at room temperature.

Figure 1 clearly shows the influence of small amounts of chlorine on the corrosion of titanium in 50 percent sulfuric acid in that 5 percent by volume of chlorine in the gaseous mixture reduced the corrosion rate of titanium approximately 100-fold. Larger additions of chlorine did not substantially reduce the corrosion rate.

## Results of Plant Tests

This information has been verified in plant tests where titanium and other

* Wyandotte Chemicals Corp., Wyandotte, Michigan.

**TABLE 1—Plant Test Results (132 Days Exposure*)**

| MATERIAL | Corrosion Rate, MPY |
|---|---|
| Hastelloy C Wrought (annealed) | 0.5 |
| Hastelloy C as welded | 0.5 |
| Hastelloy C—welded & annealed | 1.6 |
| Titanium A-70—welded | 0.1 |
| Titanium B-110-Mo | 3.9 |
| Hastelloy B—welded | >208. (sample missing) |
| Hastelloy B—welded & annealed | >206. (sample missing) |

* Samples were exposed to 50 percent $H_2SO_4$ saturated with 95 percent $Cl_2$—5 percent air having 4 ft./sec. velocity at 80 F.

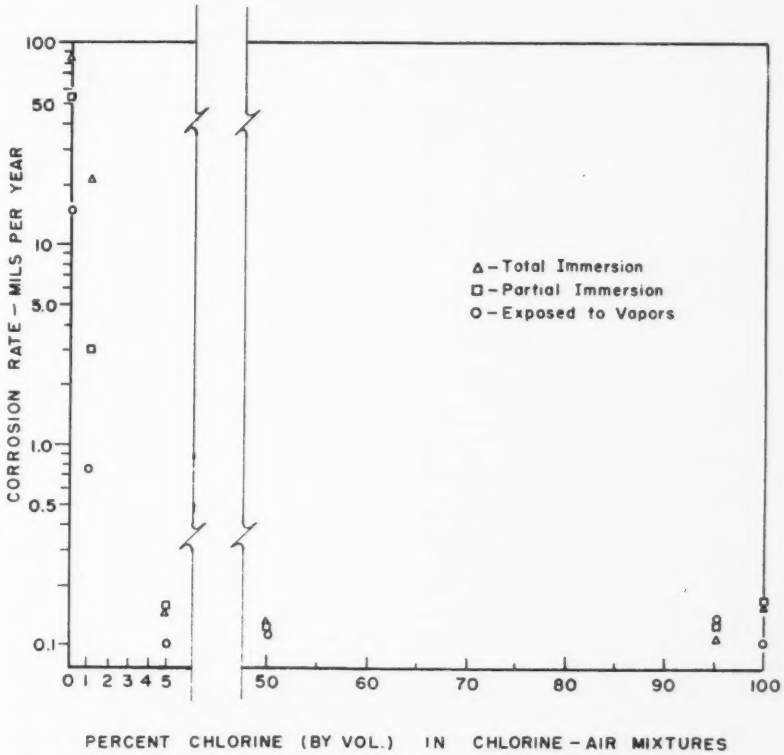


Figure 1—Corrosion rate of titanium in 50 percent sulfuric acid, saturated with chlorine—air mixtures.

**TABLE 2—Laboratory Test Results (Complete Immersion—3 Days' Exposure)**

| | CORROSION RATE—MPY | | | | |
|---|---|---|---|---|---|
| | Steel | Durimet 20 | Hastelloy C | Monel | Type 316 |
| 50% $H_2SO_4$ saturated with chlorine | 1600 | 127 | 3.4 | 465. | 175 |
| 50% $H_2SO_4$ saturated with nitrogen | 200 | 0.5 | 2.0 | 0.3 | 379 |
| 50% $H_2SO_4$ saturated with air | 2980 | 2.6 | 0.3 | 5.9 | 526 |
| 87% $H_2SO_4$ saturated with chlorine | 24.8 | <0.1 | 0.6 | 32.6 | <0.1 |
| 87% $H_2SO_4$ saturated with nitrogen | 26.7 | <0.1 | <0.1 | 25.9 | 0.2 |
| 87% $H_2SO_4$ saturated with air | 28.3 | 0.3 | 0.6 | 27.3 | 0.2 |

metals were exposed to 50 percent sulfuric acid saturated with chlorine. The data shown in Table 1 were determined on samples directly exposed in the drying acid lines, such that the velocity of acid past the samples was approximately 4 feet per second.

The results in Table 2 were obtained in a similar fashion to the information shown in Figure 1, with the difference that (1) metals other than titanium were evaluated, (2) two acid strengths were used, and (3) instead of air-chlorine mixtures, 100 percent chlorine, 100 percent nitrogen and 100 percent air were used to saturate the acid. The influence of aeration on the sulfuric acid is particularly seen in the corrosion of the steel and the Type 316 stainless steel. The absence of air and chlorine (due to nitrogen-saturation) has in many cases produced an appreciable reduction in corrosion rate. The overall suitability of Hastelloy C is clearly established for all three saturating gases.

The information in Table 2 was re-evaluated in a plant test (See Table 3). In this case a test spool of various materials was exposed to flowing 87 percent sulfuric acid saturated with chlorine (essentially 95 percent chlorine, 5 percent air) flowing at a velocity of 6 feet per second. The suitability of Hastelloy C and Type 316 stainless is evident in this case. Samples whose corrosion rate is reported as greater than a given figure were missing at the end of the test; the corrosion rate is that corresponding to complete penetration at the duration of the test.

An interesting side-light is brought out in Table 4 where the exposure of three metallic samples to partially dry chlorine gas with entrained sulfuric acid is shown, based on a 300 day test. In this case, the sample of titanium was completely missing, verifying the reported catastrophic deterioration of titanium in dry chlorine. Hastelloy C and Haynes Alloy No. 25 were exceptionally suitable in this environment.

**TABLE 3—Plant Test Results (79 Days Exposure*)**

| MATERIAL | Corrosion Rate, MPY |
|---|---|
| Hastelloy C—wrought (annealed) | 0.4 |
| Hastelloy C—as welded | 0.2 |
| Hastelloy C—welded & annealed | 1.1 |
| Titanium A-70—welded | 1.9 (crevice attack evident) |
| Type 316 wrought | 0.1 |
| Monel | > 107. (sample missing) |
| Carpenter 20 | 3.1 |
| Steel | > 52. (sample missing) |

Samples were exposed to 87 percent $H_2SO_4$ saturated with 95 percent $Cl_2$—5 percent air having 6 ft/sec. velocity at 70 F.

**TABLE 4—Plant Test Results (300 Days Exposure*)**

| MATERIAL | Corrosion Rate, MPY |
|---|---|
| Hastelloy C wrought | 0.1 |
| Haynes No. 25 wrought | < 0.1 |
| Titanium A-70 | > 39.1 (sample missing) |

Samples were exposed to partially dry chlorine gas with entrained 87 percent $H_2SO_4$ having 12 ft/sec velocity at 70 F.

The passivating effect of chlorine in the presence of water (relatively dilute sulfuric) is the apparent mechanism which retards the corrosion of titanium in the sulfuric acid.

# A Review of the Gas Condensate Well Corrosion Problem*

By D. R. FINCHER

**Abstract**

The present status of corrosion control in gas condensate wells is summarized and compared with information reported from other sources. Emphasis is placed on the "super" high pressure condensate well with shut-in pressure in excess of 5000 psi.

The following methods of applying inhibitors in gas condensate wells are reviewed: sticks, liquid lubricators, chemical pumps and pump trucks, dump bailers, chemical injection valves in the tubing, bottom hole chemical pumps, bottom hole chemical injectors, and chemical squeezes. Data are given showing the relationship between well completion method and corrosion control practices used. Other topics discussed include economic considerations, criteria of corrosiveness of wells, and selection of tubular goods. 8.4.3

## Introduction

CORROSION of equipment used in the production of gas condensate wells was recognized as a problem of economic significance as early as 1944. Through the study of this problem, much basic data were obtained which later were applied to control corrosion of other production equipment in the petroleum industry.

Through the years, the methods and means of controlling corrosion have changed to a degree. It is probable, though, that an even greater change has occurred in the gas condensate wells. In the last few years, deeper drilling has resulted in gas condensate production with surface pressures in the 10,000 psi range and bottom hole temperatures of 300 F. Safe completion and production of this type of well is of utmost importance to the operator. Corrosion is recognized as an ever present danger to the structural members of these wells, and the means and methods of controlling corrosion must be successful. Thus it is clear that a review of the basic data is in order.

## History

Much of the original work in the field of gas condensate well corrosion was accomplished by the Natural Gasoline Association of America Condensate Well Corrosion Committee. This group published a book, "Condensate Well Corrosion" in 1953, which summarized the committee's findings. This book has been one of the corrosion engineer's most used references. Each of several aspects of the problem was given attention in a chapter of the book.

## Economics

Zajac[1] presented data indicating that average uncontrolled corrosion costs were $4.27 per million cubic feet equated to the 1951 dollar value. Also, the average cost of chemical inhibition ranged from $0.03 to $1.62 per million cubic feet. These data influenced the industry to control corrosion and participate in the benefits.

The 1958 dollar value undoubtedly would change the numerical value of the uncontrolled corrosion cost, but it is believed that due to improved techniques and stable prices of inhibitors the cost of controlling corrosion has not increased proportionally. The average cost of inhibiting gas condensate wells is less than $1.00 per million cubic feet for some operators.

## Criteria of Corrosiveness

Reliable means of detecting corrosive wells prior to any extensive damage to equipment have been and are in constant demand. Bilhartz and Greenwell[2] have described the consideration of visual inspection, analysis of gas for carbon dioxide content, determination of wellhead pH, analysis of produced water for iron content and organic acids, coupon exposure, tubing caliper surveys, and study of a well's physical condition. These means of detecting corrosion have been used and when all or several are used, the reliability is of a high order.

The same criteria often are applied to determine the degree of control being experienced. The analysis of condensed water for iron content is often used in this connection. Another factor worth considering is fluctuation. When fluctuation of iron content occurs, for example from 20 ppm to 100 ppm, even if the average value is less than 50 ppm, the corrosion attack may be severe. Caliper surveys have indicated best protection of inhibited wells when iron contents do not vary over ± 5 ppm.

In the study of the physical condition of a well, the decision often must be made as to whether mass or linear velocity has the greater effect on corrosion rate. This question often is resolved by designing for the lowest practical linear velocity, with the thought that this is the safest practice. At this time, the function of velocity in corrosion attack needs to be resolved because of (1) reports of the lack of success using inhibitors in wells producing over 5 million cubic feet per day in 2-inch or 2½-inch tubing,[3] (2) the use of 1¼-inch "spaghetti" tubing in the completion of wells with the higher tubing pressures.[4]

**About the Author**

**D. R. FINCHER is Corrosion Engineer for Southern Division of Tidewater Oil Company, Houston, Texas. He received a BS in chemical engineering from Texas A and M College in 1948. After graduation, he was employed by Tidewater and has been active in corrosion work since 1949. He is chairman of NACE Subcommittee T-18.**

## Tubular Goods

In the completion of a gas condensate well the operator has the choice of J-55, N-80, P-105, or P-110 grades of carbon steel tubing. Laboratory studies indicate that the susceptibility of these materials to corrode increases in the order listed. In the higher pressure wells, use of one of the latter three grades is almost a necessity, depending upon safety factors. This fact places the higher pressure wells in a position of being more likely to experience corrosion damage.

In sour gas condensate service, the use of J-55 is deemed desirable unless special heat treatment is given to N-80. A slight reduction of safety factors is sometimes in order due to J-55 being less susceptible to sulfide stress corrosion cracking. Use of tapered strings has improved safety factors and allowed the use of J-55 to depths of 12,000 ft.

Alloy tubing has been used with success, although control of manufacture appears to be critical. Some operators have both 9 percent Cr and 9 percent Ni tubing in service and have experienced a minimum of difficulty with these materials. However, other operators have experienced cracking failures with these materials.[5]

Plastic coated tubing of all grades is available. The baked coatings being applied are phenolic, epoxy, modifications of epoxy and phenolic, phenolic with an epoxy overlay, and polyurethane. Each coating has advantages and disadvantages and should be selected for the best advantage according to environment. The cost of coated tubing is presently reduced, and some operators are coating and using inhibitors in the same well. The main disadvantage to coating tubing is that there is no entirely desirable means of determining the performance of the coating before visual examination can be made or failure occurs.

## Inhibitors

Inorganic and organic inhibitors are being used in the treatment of gas condensate wells. However, organic inhibitors were found by Waldrip[6] to be most popular. Application of inorganic inhibitors has been decreased due to the tendency to cause plugging, a minimum lasting effect, danger to personnel in handling, and pollution problems.

Numerous commercially available materials of the organic type are being used today. Application and environment apparently control the degree of success these materials enjoy. The most common problem encountered is emulsification of the well effluent. These problems often can be solved without sacrificing corrosion control.

## Application of Inhibitors

The manner in which inhibitors are used depends upon well completion.

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**TABLE 1—Well Completions and Mitigation Practices**

| Completion Method | Percent of Total Wells | Percent of Total Wells Plastic Coated | Percent of Total Wells Inhibited |
|---|---|---|---|
| Parallel Strings—Dual Completion | 8 | 0 | 8 |
| Concentric Strings | 4 | 0 | 4 |
| Single Strings—Carbon Steel | 59 | 17 | 59 |
| Single Strings—Alloys | 29 | 0 | 17 |

Wells with an annulus available to conduct inhibitor solutions are generally considered to be more easily treated. At the present time, super high pressure and multiple string parallel completions are being made. Supplying an annular space for such wells is either very expensive or impractical.

These are presently available the following means of applying inhibitors in gas condensate wells.

1. Use of sticks
2. Use of liquid lubricators
3. Use of chemical pumps and pump trucks
4. Use of dump bailers
5. Use of chemical injection valves in the tubing
6. Use of bottom hole chemical pumps
7. Use of bottom hole chemical injectors
8. Use of chemical squeezes

Stick inhibitors are available from most inhibitor companies at varying specific gravities and melting temperatures. These sticks are lubricated into the well and allowed to fall in the tubing. This method has been effective in some wells. In others the sticks have not fallen to the bottom of tubing, have not fully melted, thus resulting in plugged chokes, etc., and/or have caused the tubing to be restricted. This application is used almost entirely on wells with the annulus unavailable to conduct inhibitor solutions.

Lubricators on the other hand are used on wells that have the annulus open to conduct liquid inhibitors. Inhibitor solutions are allowed to fall through the annulus by gravity to the bottom of the tubing, and are produced in the tubing to give protection. This means is one of the oldest methods of introducing inhibitors.

Chemical pumps are used in place of lubricators on some wells where the annulus is open and continuous injection is desired. Truck mounted chemical pumps are used to treat wells with either closed or open annului. In the case of the closed annulus, the well is shut in and 20 to 40 gallons of inhibitor solution are pumped in the tubing. The assumption is made that the solution will fall to the bottom in a reasonable time. The use of pump trucks reduces investment for injection equipment if a number of wells can be serviced. Usually a corrosion control man is assigned the job of operating the truck, and the scheduling of treatment is more reliable than when the lease operator is given the added duty of applying inhibitor. The shut-in time associated with pump truck treatment sometimes causes contract gas volumes to be difficult to produce. As in the case of sticks, there is some doubt as to the depth to which the inhibitor solution falls.

Maxwell[7] described the use of a dump bailer in the treatment of gas condensate wells. Basically, a container on a wire line is run in the tubing string, and the inhibitor solution is dumped by a tripping mechanism. The inhibitor used generally contains much more active material than conventional inhibitors. The well may or may not be shut-in during this operation; if a shut-in period is required, it is of short duration. This method allows placing the inhibitor at a desired point, but only a limited volume can be dumped on a single trip of the bailer.

While completing a well, it is sometimes possible to load the annulus with inhibitor fluids and employ a bottom hole chemical injection valve. The valve is set above the packer and may or may not be wire line retrievable. By pumping inhibitor into the annulus at the surface, inhibitor solution is admitted to the tubing through the chemical injection valve in the well. One disadvantage of this completion is the expense of the large volume of inhibitor required to load the annulus. Another is the possibility of trouble with the valves. However, one operator has experienced relatively little trouble with the newer type wire line retrievable valves. Preparation of the annulus is apparently a factor in the success of this approach.

A wire line set and retrievable bottom hole chemical pump has been used with good success. This pump barrel is loaded with concentrated inhibitor. Shutting the well in for three to five minutes actuates the pump. The pump holds a limited volume of inhibitor, but the volume pumped per shut-in period can be governed by adjusting the stroke. One advantage of this tool is that less wire line work is involved. A disadvantage is that the well receives a treatment each time it is shut in, whether or not a treatment is desired.

A chemical injector is available that falls to the bottom of the tubing, ejects inhibitor, and returns to the surface. This tool is dropped when loaded with inhibitor. When it reaches bottom hole temperature, the valves open allowing the dispensing of inhibitor. The well is then opened, and the tool is produced back to the surface. This is another means of positively placing inhibitor. Difficulty can be experienced if the tubing is not free from restricting kinks or bends, and/or if the required velocity is not developed to lift the tool in its lubricator.

Poetker and Stone[8] described the "squeeze" technique of applying inhibitors in gas lift wells. The technique has been used in gas wells in much the same manner. Inhibitor solutions are pumped into the tubing and out into the formation. The well is returned to production and protection is provided for long periods of time. One operator has obtained protection of a gas well treated in this manner for as long as eight months. In the case of one sour gas condensate well, the ability of the well to produce was increased by a squeeze job. The technique is relatively new and must be fully developed before its potential is defined.

## High Pressure Wells

NACE Task Group T-1B-1 is studying the corrosion problems associated with high pressure wells. Well completion has a relationship to the corrosion control practices that can be used. The industry is approaching the problem in several ways. The manner in which one company has produced wells with tubing pressures over 5,000 psi might be typical of the industry. The breakdown of these completions and mitigation practices is shown in Table 1.

These wells, and similar wells, must be produced for several years before enough experience in operation is obtained to classify the completions and mitigation practices as satisfactory or unsatisfactory. One or all of the approaches to the problem may prove successful. The variety of approaches to the problem assures the industry that the problem is receiving the engineering effort that it deserves.

## Conclusions

The work of the NGAA Condensate Well Corrosion Committee has been of great benefit to the petroleum industry. The data assembled in the NGAA book are still useful. However, the following statement in the foreward of the book by Dr. Norman Hackerman[9] must not be overlooked: "Perhaps the single most important contribution was the conclusion that each well had some individual characteristic corrosion-wise; and, therefore the method of mitigation in each case had to be based on a careful appraisal."

Although there are still unsolved problems in controlling corrosion in gas condensate wells, much progress has been made. The new problem of high pressure wells is receiving adequate study. Generally speaking, any operator can use the prevailing practices of corrosion control of gas condensate wells and expect a material benefit.

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**Any discussions of this article not published above will appear in the December, 1958 issue**

# Corrosion Resistance of Titanium Alloys Compared With Commercially Pure Titanium*

By DAVID SCHLAIN and CHARLES B. KENAHAN


## Abstract

Titanium-8 percent manganese, titanium-5 percent aluminum-2½ percent tin, titanium-2 percent aluminum, titanium-6 percent aluminum, titanium-1 percent copper, and titanium-5 percent copper alloys are similar to commercially pure titanium in chemical and galvanic corrosion properties. These alloys are completely resistant to corrosion in synthetic ocean water, tap water, 1 percent sodium hydroxide, and 5 percent ferric chloride solutions. In sulfuric acid solutions saturated with air, the titanium alloys with the exception of those containing copper are resistant to corrosion in 5 percent solution at 35 C but corrode rapidly in 10 percent solution. At 60 C, these alloys are inert in 1 percent and corrode in 5 percent acid. The titanium-copper alloys usually are more resistant than commercially pure titanium to corrosion in sulfuric acid solutions and less resistant in hydrochloric acid. In contact with aluminum in 0.5 percent sulfuric acid saturated with air, titanium and the titanium-base alloys are the cathodic members of the couples. Titanium and titanium-base alloys are generally anodic when in contact with stainless steels in air-saturated 4.7, 9.3 and 17.5 percent sulfuric acid solutions but the galvanic corrosion rates are low. Furthermore, the chemical corrosion of titanium alloys is almost eliminated as a result of contact with stainless steel. 6.3.15


## Introduction

CONSIDERABLE ATTENTION has been given in recent years to the development of titanium alloys. Although some of the alloys are now in commercial production, little information has been published on the corrosion properties of these metals. The remarkable corrosion resistance of commercially pure titanium naturally arouses interest in the corrosion properties of titanium alloys. For this reason, the Federal Bureau of Mines investigated the chemical and galvanic corrosion behavior of a number of titanium-base alloys in typical environments.

The titanium-8 percent manganese and the titanium-5 percent aluminum-2½ percent tin alloys included in this study were commercial products. The titanium-2 percent aluminum, titanium-6 percent aluminum, titanium-1 percent copper, and titanium-5 percent copper alloys were prepared for experimental purposes by the physical metallurgy group formerly at College Park, Maryland. These alloys were made by arc-melting high-purity titanium sponge (hardness below 130 Brinell) and pure aluminum and copper shot. The commercially pure titanium used for purposes of comparison in the chemical corrosion tests also was prepared at College Park by arc-melting high-purity sponge. The titanium used in galvanic corrosion experiments was a commercial product, consolidated by arc-melting.[1] Other metals used in galvanic couples included commercially pure aluminum (2S-0), commercially pure magnesium, magnesium alloy FS1, and Types 302 and 20Cr-29Ni stainless steels.

## Test Procedures

Metal specimens received a preliminary polish with wet silicon carbide paper on a mechanical polisher. Immediately before immerson they were surfaced by hand with 3/0 emery cloth, rubbed with wet pumice, washed with water, dried with acetone, and weighed. Synthetic ocean water[2] was prepared according to a formula developed by the ASTM[1]; tap water[3] was from College Park, Maryland.

Schlain

Kenahan


**DAVID SCHLAIN**—Chemical engineer, Bureau of Mines, U. S. Department of Interior, Region V, Division of Mineral Technology, College Park, Maryland. He received BS and MS degrees from University of Pennsylvania and a PhD in chemical engineering from University of Maryland. His research interests include process metallurgy, electrodeposition, passivity and corrosion phenomena, applications of ultrasonics to metallurgy. He is a member of American Chemical Society, Electrochemical Society, and American Society for Metals.

**CHARLES B. KENAHAN**—Chemist, Bureau of Mines, U. S. Department of Interior, Region V, Division of Mineral Technology, College Park, Maryland. He received a BS in chemistry from Kings College in 1950. From 1951 to 1953 he was employed by the Battery Section of the Naval Ordnance Laboratory, and from 1953 to 1955, he conducted an investigation of the corrosion properties of titanium and zirconium for the Bureau of Mines. At present, Mr. Kenahan is engaged in the application of ultrasonics to metallurgical problems.


Chemical corrosion tests were conducted according to recommendations of the American Society for Testing Materials[2] and were generally six days in length. Solution temperatures were 35 or 60 C. Experiments were conducted in 1-liter Erlenmeyer flasks with loosely fitting aerator-condenser assemblies. Each vessel contained two specimens and 750 ml of corrodant. Air was passed through the solution for one hour before the specimens were immersed and continuously throughout the experiment (100 ml per minute).

Galvanic corrosion experiments were conducted at 35 C in stoppered bottles with a continuous flow of air (50 ml per minute) and lasted 15 days. In every experiment, two specimens of each of the two metals involved were inserted through slits in small rubber stoppers which fitted tightly in holes in the large bottle stopper. This formed gas-tight seals, yet permitted external connections. Each specimen had 0.11 square decimeter of surface exposed to the corrodant. One pair of dissimilar specimens was connected through a 1-ohm (± 1 percent) resistance; the other two specimens were not coupled. Galvanic currents flowing through the couples were determined by measuring voltage drops across the resistance and applying Ohm's law. The voltages were measured with a millivoltmeter, with a potentiometer and a galvanometer, or with a potentiometer and an electronic microvoltmeter used as a null indicator.

Galvanic corrosion rates were calculated from average galvanic currents by applying Faraday's law. Galvanic corrosion was always averaged for the full 15-day period, even in those instances when there was no galvanic current during part of the period. The weight-losses of the coupled and uncoupled specimens were determined and used in calculating total corrosion rates. The electrode potentials of each uncoupled specimen and of the couple were measured with an L and N type K-2 potentiometer, a saturated calomel electrode, and a saturated potassium chloride bridge. The positions of the electrode potentials of the various metals on the saturated calomel electrode scale are shown on the chart.

## Discussion

### *Synthetic Ocean Water, Sodium Hydroxide, and Ferric Chloride Solutions*

Like commercially pure titanium, the titanium-base alloys are completely resistant to chemical and galvanic attack in synthetic ocean water (Tables 1 and 2). The single electrode potentials of the titanium alloys were always much more

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(1) Impurity content, in percent: C, 0.044; $N_2$, 0.027; $O_2$, 0.1; Fe, 0.13; Mn, 0.076; W, 0.02 max; Si, 0.04 max.

(2) Composition in grams per liter: NaCl, 24.53; $MgCl_2 \cdot 6H_2O$, 11.11; $Na_2SO_4$, 4.09; $CaCl_2$, 1.16; KCl, 0.695; $NaHCO_3$, 0.201; KBr, 0.101; $H_3BO_3$, 0.027; $SrCl_2 \cdot 6H_2O$, 0.042; NaF, 0.003.

(3) Analysis, in parts per million: Hardness (total) 31-44, alkalinity (total) 15-30, alkalinity $CO_3$ 3-6, alkalinity $HCO_3$ 10-24, $SiO_2$ 0.2-2.8, Ca 7-19, Mg 0.2-3, $SO_4$ 7-13, fluoride 0.7-1.0, Fe (total) 0.0, $Fe_2O_3$ and $Al_2O_3$ 0-5, $Cl_2$ (starch KI) 1, Mn 0.0, $NH_3$ (free) 0.0, solids 50-100, chlorides 2-7.5. Dissolved oxygen, percent saturated 87-100; pH 8.7. Information supplied by the Washington Suburban Sanitary Commission, Hyattsville, Maryland.

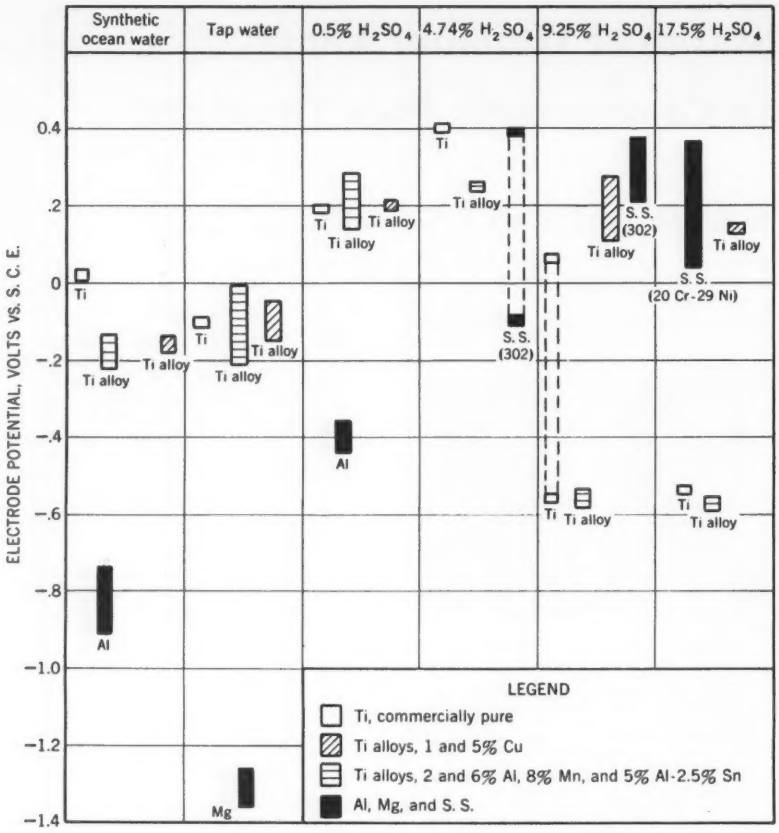


Figure 1—Single electrode potentials of metals in solutions with flow of air at 35 C. Potential is referred to saturated calomel electrode.

**TABLE 1—Titanium and Titanium Alloys in Various Corrodants***

| Solution | Temp., Degrees C | CORROSION RATE, MILS PER YEAR | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Ti, Comm. Pure | Ti-8% Mn[a] | Ti-5% Al-2½% Sn | Ti-2% Al | Ti-6% Al | Ti-1% Cu | Ti-5% Cu |
| Synthetic ocean water | 35 | 0.0[a,b] | 0.0[b] | 0.0[a,b] | 0.0[a,b] | 0.0[b] | 0.0 | 0.0 |
| Sodium hydroxide, 1 percent | 60 | ..... | 0.0 | 0.0 | .... | .... | .... | .... |
| Ferric chloride, 5 percent | 60 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | .... |
| Sulfuric acid, 1 percent | 60 | 0.0 | 0.1 | 0.5 | 0.3 | .... | .... | .... |
| Sulfuric acid, 3 percent | 35 | 0.2[c] | 0.2 | .... | 0.3 | 4.4 | .... | .... |
| | 60 | 0.5[c] | 48.5[d] | .... | 31.4 | 60.9 | 10.1 | 0.7 |
| Sulfuric acid, 5 percent | 35 | 3.2 | 0.2 | [e] | 0.3 | 0.5 | .... | .... |
| | 60 | 28.8 | 108 | 95.5 | [f] | 99.7 | 24.0 | 5.7 |
| Sulfuric acid, 10 percent | 35 | 53.3 | 91.2 | 53.8 | 61.4 | 69.0 | 11.4 | 0.5 |
| Sulfuric acid, 50 percent | 35 | 107[c] | .... | .... | .... | .... | 29.7[g] | 14.2 |
| Sulfuric acid, 96.5 percent | 35 | 209[c] | .... | .... | .... | .... | 151 | 187 |
| Hydrochloric acid, 4 percent | 35 | 0.0 | 0.2 | 13.4[a] | 0.3 | 12.0 | .... | .... |
| | 60 | [e] | 41.1 | 79.4[a] | 79.2 | 82.5 | 57.4 | 27.5 |
| Hydrochloric acid, 10 percent | 35 | 42.4[c] | .... | .... | .... | .... | 118 | 160 |
| | 60 | 351[c] | .... | .... | .... | .... | 288 | 205 |
| Hydrochloric acid, 20 percent | 35 | 126[c] | .... | .... | .... | .... | 1606[g] | 870 |
| Oxalic acid, 1 percent | 35 | 0.4 | 0.4 | 9.2 | 0.5 | [e] | .... | .... |
| | 60 | 59.0 | 80.8 | 52.8 | 52.0 | 94.8 | .... | .... |

* Flow of air through solution, 100 ml per minute; 6-day experiments; 2 replicates.

[a] Number of replicates, 4.

[b] Experiment lasted 30 days.

[c] Taken from the literature (references 3 and 4). These data were obtained with specimens cut from sheets consolidated by powder metallurgy techniques.

[d] This value is the average for two specimens; two other specimens were passive, average corrosion rate 0.4 mpy.

[e] Number of replicates, 2; one inactive, corrosion rate 0.3 to 1.3 mpy; other active, corrosion rate 20 to 32 mpy.

[f] Number of replicates, 2; one 30 mpy, other 101 mpy.

[g] Experiment lasted 3 days.

noble than that of aluminum (see Figure 1); when coupled with commercially pure aluminum, the titanium alloys were always the cathodic (non-corroding) members of the couples. Yet there was little galvanic corrosion of aluminum. Single specimens of aluminum also were resistant to corrosion in synthetic ocean water.

The titanium-base alloys are similar to commercially pure titanium in being completely resistant to chemical attack in 5 percent ferric chloride solution (Table 1). The titanium-8 percent manganese and titanium-5 percent aluminum-2½ percent tin alloys are resistant to corrosion in 1-percent sodium hydroxide (Table 1).

*Tap Water*

Titanium and titanium-base alloys are inert in tap water (Table 3). Single specimens of magnesium and magnesium alloy FSl corroded in tap water, and the coupling of these metals with titanium or with any of the titanium alloys resulted in even higher corrosion rates. These high rates of galvanic corrosion are consistent with the position of magnesium relative to that of the titanium alloys on the electrode potential chart. Corrosion of magnesium and magnesium alloy FSl occurred chiefly in pits and at the tips of the specimens.

*Sulfuric Acid Solutions*

Commercially pure titanium and the titanium-8 percent manganese, titanium-2 percent aluminum, titanium-6 percent aluminum, and titanium-5 percent aluminum-2½ percent tin alloys were resistant to chemical attack in the less concentrated sulfuric acid solutions. These alloys all corroded rapidly, however, in 5-percent acid at 60 C and in 10-percent acid at 35 C (Table 1). In some instances commercially pure titanium appeared to be somewhat more resistant than the alloys but in 5-percent sulfuric acid at 35 C it was slightly less resistant.

The data for titanium-8 percent manganese alloy in sulfuric acid are usually in agreement with those of Golden, Acherman, and Schlain.[5] The major variations occur in 3-percent sulfuric acid at 60 C (Golden, 5.33 mpy), and in 5-percent sulfuric acid at 35 C (Golden, 4.1 mpy). These are areas of borderline passivity and erratic results are to be expected.

The titanium-1 percent copper alloy was more resistant than commercially pure titanium to chemical corrosion in 10 and 50 percent sulfuric acid solutions at 35 C and the titanium-5 percent copper alloy was more resistant in 5, 10, and 50 percent acid solutions. The titanium-1 percent copper alloy appears to corrode more than titanium in 3 percent sulfuric acid solution at 60 C but is more resistant than the titanium alloys without copper. These data show that the addition of copper increases the corrosion resistance of titanium in sulfuric acid solutions. This conclusion is in general agreement with that of Rudiger, Fischer, and Knorr[6] who tested titanium alloys containing 2 to 10 percent copper in boiling 15-percent sulfuric acid.

In electrical contact with aluminum and immersed in 0.5 percent (0.1N) sulfuric acid saturated with air, commercially pure titanium and the titanium alloys were always the cathodic members of the couples (Table 4). The galvanic corrosion of aluminum was rapid in every instance. This is consistent with

**TABLE 2—Galvanic Corrosion of Titanium Alloy-Aluminum (2S-O) Couples in Synthetic Ocean Water, 35 C***

| Titanium Alloy | Corrosion of Aluminum, mpy | | |
|---|---|---|---|
| | Galvanic[a] (Calculated from Current) | Based on Weight Loss | |
| | | Coupled | Uncoupled |
| Commercially pure Ti. . . . | 0.1 | 0.6 | 0.1 |
| Ti—8% Mn. . | .3 | 2.3 | .3 |
| Ti—5% Al—2½% Sn. . . | .1 | .9 | .2 |
| Ti—2% Al. . . | .1 | 1.1 | .4 |
| Ti—6% Al. . . | .2 | .8 | .4 |
| Ti—1% Cu. . . | .1 | .9 | .3 |
| Ti—5% Cu. . . | .4 | .8 | .4 |

* Flow of air through solution, 50 ml per minute; 15-day experiments.

**Note:** Titanium alloys were inert in all experiments; corrosion rate, 0.0 mpy.

[a] Galvanic current flowed through the couples only during the first two to five days after immersion. Galvanic corrosion rates were averaged for 15 days.

**TABLE 3—Galvanic Corrosion of Titanium Alloy-Magnesium Alloy (FS1) Couples in Tap Water (College Park, Md.), 35 C***

| Titanium Alloy | Corrosion of Magnesium, mpy | | |
|---|---|---|---|
| | Galvanic (Calculated from Current) | Based on Weight Loss | |
| | | Coupled | Uncoupled |
| Commercially pure Ti. . . . | 21.5 | 29.3 | 8.7 |
| Ti—8% Mn. . | 7.1 | 18.5 | 5.4 |
| Ti—5% Al—2½% Sn[a]. . | 7.0 | 14.4 | 4.3 |
| Ti—2% Al. . . | 28.2 | 41.6 | 11.6 |
| Ti—6% Al. . . | 18.6 | 28.0 | 10.7 |
| Ti—1% Cu. . . | 14.6 | 24.3 | 8.8 |
| Ti—5% Cu. . . | 23.5 | 35.2 | 7.9 |

* Flow of air through solution, 50 ml per minute; 15-day experiments.

**Note:** Titanium alloys were inert in all experiments; corrosion rate, 0.0. mpy.

[a] Commercially pure magnesium.

the fact that the single electrode potentials of titanium and the titanium alloys are always more noble than that of aluminum (see Figure 1). However, because aluminum tends to have a negative difference effect, contact with titanium does not greatly increase the total corrosion rate of aluminum. Although single specimens of titanium alloys resist corrosion in this solution and although titanium alloys are always the cathodic members of the titanium alloy-aluminum couples, contact with aluminum generally causes the titanium alloys to corrode slowly. This type of attack is known as cathodic corrosion, and other instances of its occurrence have been reported.[7]

Titanium alloys are generally the anodic members of couples with stainless steels (Table 5) when immersed in 4.7, 9.3, and 17.5 percent (1, 2, and 4N) sulfuric acid solutions with a flow of air. There are exceptions to this generalization. Coupled with Type 302 stainless steel in 1N acid, commercially pure titanium was cathodic during the entire experiment. Titanium-8 percent manganese alloy became cathodic after a period of immersion in this environment. The titanium-copper alloys were cathodic when coupled with stainless steel in 2N acid. The direction of flow of current in these couples is consistent with the relative values for the electrode potentials of the single specimens (see Figure 1). However, the rates of galvanic corrosion of the titanium alloys are small in view of the large differences between the single electrode potentials of the titanium alloys and the stainless steels. The total corrosion rates of the stainless steels were not affected by contact with titanium. Corrosion of Type 302 stainless steel in 1 and 2N acid sometimes was definitely erratic.

**TABLE 4—Galvanic Corrosion of Titanium Alloy-Aluminum (2S-O) Couples in 0.5 Percent (0.1N) Sulfuric Acid Solution, 35 C***

| Titanium Alloys | Corrosion of Aluminum, mpy | | | Corrosion of Titanium Alloy, mpy | |
|---|---|---|---|---|---|
| | Galvanic (Calculated from Current) | Based on Weight Loss | | Based on Weight Loss | |
| | | Coupled | Uncoupled | Coupled | Uncoupled |
| Commercially pure Ti. . . . . | 23.5 | 47.3 | 43.0 | 0.8 | 0.1 |
| Ti—8% Mn. . . . . | 10.9 | 36.3 | 30.2 | 1.7 | .0 |
| Ti—5% Al—2½% Sn. . . . . | 17.0 | 46.0 | 41.3 | .7 | .1 |
| Ti—2% Al. . . . . | 22.9 | 46.4 | 41.5 | .4 | .0 |
| Ti—6% Al. . . . . | 14.8 | 43.4 | 38.8 | 1.3 | .1 |
| Ti—1% Cu. . . . . | 27.1 | 51.7 | 43.9 | .1 | .0 |
| Ti—5% Cu. . . . . | 27.5 | 49.0 | 39.3 | .2 | .0 |

* Flow of air through solution, 50 ml per minute; 15-day experiments.

Single specimens of the titanium-8 percent manganese alloy corroded in 4.7 percent acid. This does not agree with the very low corrosion rate obtained in 5 percent acid during chemical corrosion tests (Table 1). Such variation in behavior probably is indicative of borderline passivity. Corrosion rates for single speciments of the titanium alloys in 9.25 percent sulfuric acid are in good agreement with results of chemical corrosion tests (Table 1, 10 percent acid).

In those solutions in which titanium normally undergoes chemical corrosion and is less noble than the stainless steels, coupling with a stainless steel virtually eliminated the chemical corrosion of titanium (Table 5). Uncoupled specimens of titanium present in the same vessels corroded at the usual rates. Hence, the inertness of the coupled titanium specimens was not caused by the presence of the ferric ions but was evidently the result of anodic polarization of titanium.

*Hydrochloric Acid Solutions*

Titanium, the titanium-8 percent manganese and the titanium-2 percent aluminum alloys were resistant in 4 percent hydrochloric acid at 35 C (Table 1). The titanium-5 percent aluminum-2½ percent tin and the titanium-6 precent aluminum alloys were moderately active in this environment. All of these alloys were active in 4 percent hydrochloric acid at 60 C. The titanium-copper alloys corroded rapidly in 4, 10, and 20 percent solutions. The addition of copper decreases the corrosion resistance of titanium in hydrochloric acid solutions. This agrees with the generalization of Rudiger, Fischer, and Knorr[6] who worked with boiling 10 percent hydrochloric acid.

*Oxalic Acid*

Commercially pure titanium, titanium-8 percent manganese, titanium-5 percent aluminum-2½ percent tin, and the titanium-aluminum alloys corroded in 1 percent oxalic acid at 60 C (Table 1). At 35 C, commercialy pure titanium, titanium-8 percent manganese, and titanium-2 percent aluminum were resistant in this solution.

*Air-Free Acid Solutions*

Some experiments were carried out with sulfuric, hydrochloric, and oxalic acid solutions from which the air was removed with a flow of helium. In such solutions, corrosion of titanium and of the titanium alloys generally occurs at lower acid concentrations and temperatures than in air-saturated solutions because the protective oxide film cannot be maintained in the absence of air. For example, in the chemical corrosion tests commercially pure titanium, titanium-5 percent aluminum-2½ percent tin, titanium-8 percent manganese, and the titanium-aluminum alloys became active in air-free 1 percent sulfuric acid at 60 C and in air-free 3 percent acid at 35 C (16 to 113 mpy). The removal of air from 5 percent sulfuric acid at 35 C resulted in a higher corrosion rate for commercially pure titanium (18 mpy) and caused the titanium alloys to become active (27 to 42 mpy). In 5 percent sulfuric acid at 60 C the removal of air caused the already active titanium and titanium alloys to corrode even more rapidly (114 to 269 mpy). Titanium and the alloys were all active in 4 percent hydrochloric acid (10 to 15 mpy) and in 1 percent oxalic acid (24 to 52 mpy) at 35 C.

In every instance, electrode potentials were less noble in air-free sulfuric acid solutions than in solutions saturated with air. When titanium, titanium-manganese, titanium-aluminum-tin, or titanium-aluminum alloys were coupled with aluminum in air-free 0.5 percent sulfuric acid they became anodic after an initial period of immersion and corroded by galvanic action at moderate rates (3 to 7 mpy). Titanium and the titanium alloys in contact with stainless steel in air-free 9.25 percent sulfuric acid solution were anodic just as they were in solution saturated with air. However, in the air-free solution the galvanic corrosion of the titanium alloys was much more rapid (17 to 36 mpy).

## Conclusions

Like commercially pure titanium, the titanium-base alloys included in this investigation are completely resistant to corrosion in synthetic ocean water, tap water, 1 percent sodium hydroxide, and 5 percent ferric chloride solutions. Contact with aluminum in synthetic ocean water or with magnesium in tap water does not affect this resistance.

In sulfuric acid solutions, the titanium-8 percent manganese, titanium-5 percent aluminum-2½ percent tin, titanium-2 percent aluminum, and titanium-6 percent aluminum alloys have corrosion properties similar to those of titanium. In solutions saturated with air at 60 C the passivity of the alloys breaks down in acid concentrations between 1 and 3 percent; at 35 C, it breaks down in acid concentrations between 5 and 10 percent. When corrosion occurs, the

**TABLE 5—Galvanic Corrosion of Titanium Alloy—Stainless Steel Couples in Sulfuric Acid Solutions at 35 C***

| Titanium Alloy | Stainless Steel | Anodic Metal | Galvanic Corrosion, mpy (Calc. from Current) | CORROSION RATE, MPY (Based on Weight Loss) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Titanium Alloy | | Stainless Steel | |
| | | | | Coupled | Uncoupled | Coupled | Uncoupled |
| **4.74 PERCENT (1N) SULFURIC ACID** | | | | | | | |
| Commercially pure Ti | Type 302 | S.S. | 1.5 | 0.7 | 0.2 | ..... | ..... |
| Ti—8% Mn | Type 302 | S.S, Ti[a] | 0.6, 0.5 | 0.7 | 18.3 | 21.7 | 26.7 |
| **9.25 PERCENT (2N) SULFURIC ACID** | | | | | | | |
| Commercially pure Ti | Type 302 | Ti | 0.5 | 0.2 | 40.8 | 4.1 | 0.1 |
| Ti—8% Nn | Type 302 | Ti | 0.7 | 0.2 | 76.3 | 0.4 | 0.0 |
| Ti—5% Al—2½% Sn | Type 302 | Ti | 2.2 | 2.3 | 75.1 | 25.3 | 27.0 |
| Ti—2% Al | Type 302 | Ti | 0.5 | 0.2 | 77.8 | 1.1 | 0.1 |
| Ti—6% Al | Type 302 | Ti | 0.7 | 0.6 | 87.7 | 7.0 | 0.1 |
| Ti—1% Cu | Type 302 | Ti, S.S.[b] | 0.2, 1.4 | 0.5 | 18.1 | 15.7 | 15.2 |
| Ti—5% Cu | Type 302 | S.S. | 4.8 | 0.7 | 0.1 | 16.1 | 15.6 |
| **17.50 PERCENT (4N) SULFURIC ACID** | | | | | | | |
| Commercially pure Ti | 20Cr—29Ni | Ti | 0.9 | 0.1 | 84.3 | 0.1 | 0.0 |
| Ti—8% Mn | 20Cr—29Ni | Ti | 0.7 | 0.2 | 154.3 | 0.1 | 0.1 |
| Ti—2% Al | 20Cr—29Ni | Ti | 0.9 | 0.0 | 132.2 | 0.2 | 0.0 |
| Ti—6% Al | 20Cr—29Ni | Ti | 1.0 | 0.7 | 139.6 | 0.2 | 0.0 |
| Ti—1% Cu | 20Cr—29Ni | Ti[c] | 0.0 | 0.1 | 40.9 | 0.1 | 0.0 |
| Ti—5% Cu | 20Cr—29Ni | Ti[c] | 0.0 | 0.3 | 13.6 | 0.1 | 0.1 |

* Flow of air through solution, 50 ml per minute; 15-day experiments.

[a] Titanium was the anodic member of the couple during the first day and the last nine days of the experiment. Stainless steel was anodic the remainder of the time.

[b] Titanium was the anodic member of the couple during the first day.

[c] Titanium alloy was anodic during the first four hours after immersion. No current was detected during the remainder of experiment.

rates for the alloys are usually somewhat higher than those for commercially pure titanium. The addition of 5 percent copper increases the corrosion resistance of titanium in sulfuric acid solutions. The titanium-5 percent copper alloy is resistant in 3 percent sulfuric acid at 60 C and in 10 percent acid at 35 C. It corrodes much less than titanium in 5 percent acid at 60 C and in 50 percent acid at 35 C. The titanium-1 percent copper alloy corrodes in 3 percent acid at 60 C, although commercially pure titanium is resistant. This alloy corrodes less rapidly than titanium in air-saturated 10, 50, and 96.5 percent sulfuric acid solutions at 35 C.

Commercially pure titanium and the titanium-8 percent manganese and titanium-2 percent aluminum alloys are resistant to corrosion in air-saturated 4 percent hydrochloric acid and in 1 percent oxalic acid solutions at 35 C. The titanium-5 percent aluminum-2½ percent tin alloy corrodes at moderate rates in these environments. The titanium-6 percent aluminum alloy corrodes at a moderate rate in 4 percent hydrochloric acid but is sometimes passive in 1 percent oxalic acid. Titanium and the titanium alloys corrode in these solutions at 60 C.

Titanium and the titanium alloys do not undergo galvanic corrosion when in contact with aluminum in air-saturated 0.5 percent sulfuric acid solution at 35 C but there is some cathodic corrosion.

In air-saturated 4.7, 9.3, and 17.5 percent sulfuric acid solutions at 35 C, titanium and titanium alloys are generally anodic when coupled with stainless steels but the galvanic corrosion rates are very low. Furthermore, contact with stainless steel virtually eliminates chemical corrosion of titanium and the titanium alloys.

When air is removed from sulfuric, hydrochloric, or oxalic acid solutions, titanium and the titanium alloys corrode at lower acid concentrations and temperatures because the protective oxide film cannot be maintained in such solutions.

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**Any discussions of this article not published above will appear in the December, 1958 issue**

# Effect of the Concentration of Various Salts on the Dissolution of Cadmium in Air-Saturated Solutions*

By CHARLES J. BOONE and CECIL C. LYNCH


## Abstract

The initial rate of dissolution of cadmium in various concentrations of carbon dioxide-free, air-saturated neutral salt solutions at 25 C was examined polarographically. The salts employed were potassium chloride, sodium chloride, barium chloride, potassium bromide, sodium bromide, potassium iodide, sodium iodide, sodium perchlorate, and barium perchlorate. The experiments were conducted in such a manner that the only variable was the concentration of salt in the solutions.

The order of reaction due to the salt was calculated at 25 C for the initial rate of dissolution of cadmium for each of the above salts. The nature of the anion was shown to have a much greater effect on the rate than does the nature of the cation. The perchlorate ion appears to act as an inhibitor and the iodide salts to have a maximum in the corrosion rate versus concentration curves. These results may be explained on the basis of anion polarization 4.3.6


## Introduction

VARIOUS INVESTIGATORS have observed the effect of the concentration of salt solutions on the rate of corrosion of metals.[1-7] Their data were obtained, however, over long periods of time during which the products of corrosion greatly influence the rate of dissolution of the metal. It has been known for some time that the rate for the initial period of corrosion is much faster than that in the latter stages where films of various kinds form on the corroding metal. These films tend to slow the corrosion rate and account for the decrease in the rate of corrosion as the attack proceeds.

Relatively little has been done to investigate the initial rate of corrosion by measuring the rate of the dissolution of the metal during the early stages of corrosion. Rauch and Kolb[8] investigated the corrosion of copper in salt solutions over a period of one hour and found that the corrosion rate varied linearly with time over this period.

Hill[9] found that the early stages of corrosion of copper in aqueous potassium chloride solutions was of the first order with respect to the oxygen and hydrogen ion concentration. He also found that subsequent to the initial reaction, the rate became parabolic, then logarithmic, owing to a change in mechanism.

Tödt[10] found that the initial rate of the dissolution of iron in various media was very rapid as compared to the latter stages of corrosion. Shatalov[11] observed a rapid rate of corrosion of cadmium in acid solutions during the initial period which soon decreased and became constant due to the formation of a film of corrosion products on the surface of the cadmium.

The primary aim of this work is to elucidate the kinetics of the initial stage of the corrosion of cadmium by measuring the rate of dissolution of cadmium in various concentrations of neutral salt solutions. This will afford a means of studying the effect of cations and anions on the initial stage of the dissolution.

## Theory

Temperature, pH, history of the metal being corroded, velocity of the solution, and oxygen concentration as well as the nature and concentration of salt have an appreciable effect on the rate of corrosion of metals in salts solutions. If all the variables other than the concentration of the salt solution are kept constant during the course of the investigation, the effect of the cations and anions as well as of the concentration of the salt solution on the initial stage of the dissolution of cadmium can be studied. The rate of corrosion will then depend upon the nature of the salt being studied and upon the concentration or ionic strength of this salt solution. Thus,

$$S_o = K\mu^n \qquad (1)$$

where $S_o$ = initial rate of corrosion
K = a constant
$\mu$ = ionic strength of the solution being studied
n = order of reaction due to the salt

The initial rate of corrosion may be obtained by measuring the change in concentration of the cadmium in the salt solution with time. The initial slope of the curve obtained by plotting the cadmium concentration versus time gives the initial rate of corrosion. Then,

$$\text{Log } S_o = K' + n \text{ Log } \mu \qquad (2)$$

The plot of Log $S_o$ versus Log $\mu$ should give a straight line the slope of which is equal to n, the order of reaction due to the salt being studied.

Boone

Lynch

**CHARLES J. BOONE has been engaged in analytical research for the American Viscose Corporation at Marcus Hook, Pennsylvania, since 1951. He received an AB degree from Temple University in 1951, an MS degree from the University of Pennsylvania in 1952, and a PhD degree from the University of Delaware in 1957.**

**CECIL C. LYNCH is Professor of Chemistry at the University of Delaware, Newark, Delaware. His principal fields of research include potentiometric studies in aqueous and low dielectric media, phase systems, and polarographic kinetic studies. He received BS and MS degrees from the University of Delaware and a PhD from Columbia University.**

## Experimental

Reagent grade salts were used throughout this work. When tests indicated a salt to be of insufficient purity, the salt was purified by repeated recrystallizations. Reagent grade cadmium in the rod form was used as a source of cadmium. The rods were machined into cylinders 5 cm long and about 0.8 cm in diameter. These were annealed by placing the cadmium cylinders in an oven at 295 to 300 C under an atmosphere of nitrogen. The temperature was slowly lowered to room temperature over a period of three days.

The cadmium bar was fitted to a stainless steel stirring rod which could be rotated at various speeds by an electric motor. Five hundred ml of the salt solution being studied were placed in a one liter three neck round bottom flask. The flask was kept in a constant temperature bath at 25 C during the course of each experiment. Carbon dioxide free air was passed through the solution at a rate of about 75 ml per minute through a fritted glass distributing head. The cadmium bar, the exposed surface of which was regulated by adjusting Tygon tubing over the bar, was placed in the salt solution after one hour of gassing with carbon dioxide free air. The Tygon tubing also served to protect the stainless steel stirring rod from the solution.

The cadmium bar was first polished with emery cloth and then with Crocus cloth prior to each experiment. The rpm of the stirrer was adjusted to 2350 ± 50 rpm. At 5 or 15 minute intervals, depending on the rate of dissolution, 10 ml aliquots of salt solution were withdrawn and the cadmium concentration determined polarographically using a Leeds and Northrup Electro-Chemograph, Type E. The cadmium was corroded for 40 minute periods in some cases and 120 minute periods in others where the rate of dissolution was slower.

## Discussion

Preliminary experiments indicated that over a pH range of 7.0 to 9.0, the initial rate of the dissolution of cadmium is independent of the initial pH of the salt solution. Other investigators also have shown that over a limited pH range, the rate of corrosion of various metals is independent of pH. Mortensen[12] for

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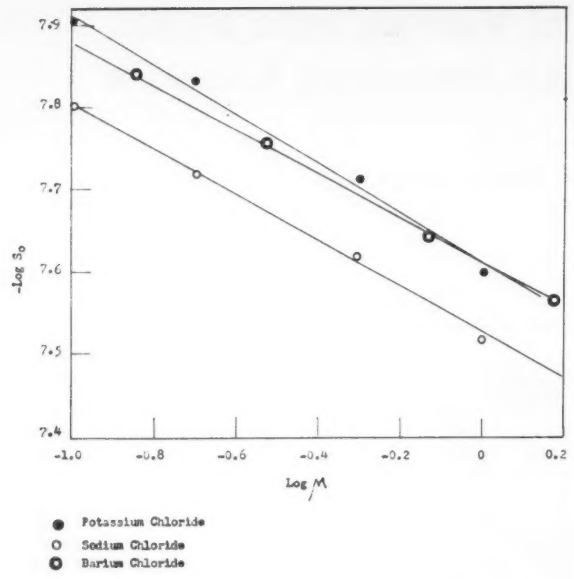


Figure 1—Kinetics of the dissolution of cadmium in carbon dioxide-free, air-saturated chloride salt solutions at 25 C.

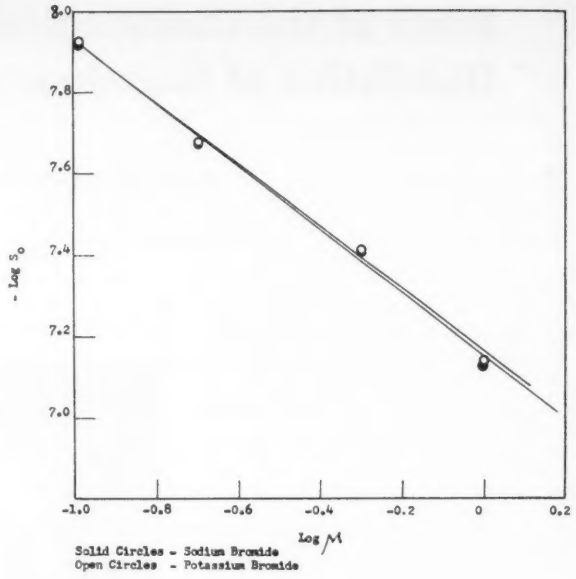


Figure 2—Kinetics of the dissolution of cadmium in carbon dioxide-free, air-saturated bromide salt solution at 25 C.

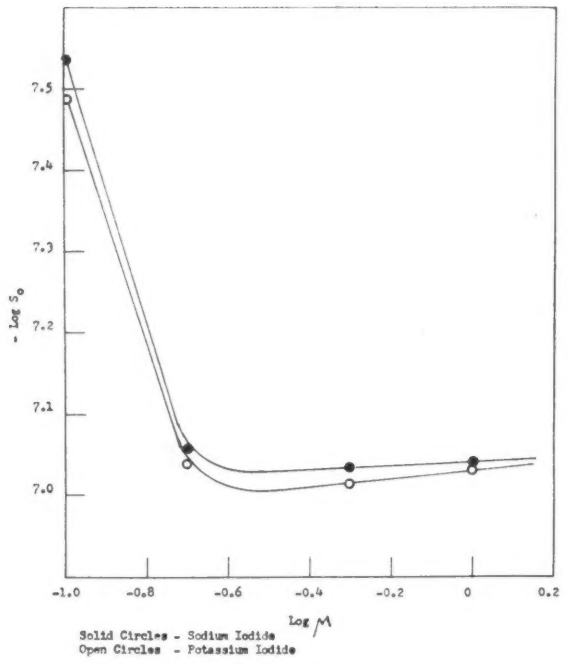


Figure 3—Kinetics of the dissolution of cadmium in carbon dioxide-free, air-saturated iodide salt solutions at 25 C.

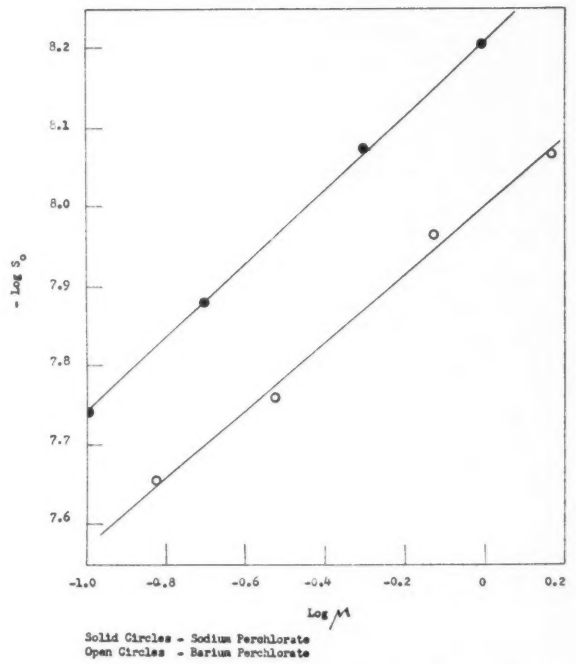


Figure 4—Kinetics of the dissolution of cadmium in carbon dioxide-free, air-saturated perchlorate salt solutions at 25 C.

example, has studied the rate of corrosion of iron over a pH range of 4 to 9. This indicates that although the pH of the carbon dioxide-free, air-saturated salt solutions increases with time during the course of corrosion, this increase in pH does not influence the initial rate of the dissolution of cadmium in these solutions.

Preliminary experiments showed that the speed of rotation of the cadmium bar during the experiments should be in the range of 1800 to 2600 rpm in order to yield reproducible results. Below 1800 rpm, results were lower and also the precision of the measurements decreased. Hence, in the kinetic studies of the dissolution of cadmium in neutral salt solutions, the speed of the rotation of the cadmium bar was kept at 2350 ± 50 rpm.

During the course of the experiments concerned with the initial rate of dissolution of cadmium in neutral salt solutions, the variables which affect the initial rate of dissolution were controlled to such an extent that their effects can be regarded as being constant. As explained above, the effects of pH and the speed of rotation of the cadmium bar over the range encountered in the experiments can be regarded as being constant. The effect

**TABLE 1—Kinetics of the Dissolution of Cadmium in Carbon Dioxide-Free Air-Saturated Salt Solutions at 25 C**

| μ | K x $10^8$ | $S_o$* | —Log $S_o$ | Log μ |
|---|---|---|---|---|
| **Potassium Chloride** n** = 0.288 | | | | |
| 1.000 | 3.03 | 3.03 | 7.518 | 0.000 |
| 0.500 | 2.93 | 2.40 | 7.620 | —0.301 |
| 0.200 | 3.03 | 1.91 | 7.719 | —0.699 |
| 0.100 | 3.05 | 1.57 | 7.803 | —1.000 |
| **Sodium Chloride** n** = 0.306 | | | | |
| 1.000 | 2.51 | 2.51 | 7.601 | 0.000 |
| 0.500 | 2.39 | 1.93 | 7.714 | —0.301 |
| 0.200 | 2.39 | 1.46 | 7.835 | —0.699 |
| 0.100 | 2.52 | 1.25 | 7.904 | —1.000 |
| **Barium Chloride** n** = 0.272 | | | | |
| 1.500 | 2.41 | 2.70 | 7.569 | 0.176 |
| 0.75 | 2.46 | 2.27 | 7.644 | —0.125 |
| 0.300 | 2.41 | 1.74 | 7.759 | —0.523 |
| 0.150 | 2.41 | 1.44 | 7.841 | —0.824 |
| **Potassium Bromide** n** = 0.760 | | | | |
| 1.000 | 7.24 | 7.24 | 7.140 | 0.000 |
| 0.500 | 6.54 | 3.86 | 7.413 | —0.301 |
| 0.200 | 7.13 | 2.10 | 7.678 | —0.699 |
| 0.100 | 6.74 | 1.17 | 7.931 | —1.000 |
| **Sodium Bromide** n** = 0.779 | | | | |
| 1.000 | 7.34 | 7.34 | 7.134 | 0.000 |
| 0.500 | 6.65 | 3.89 | 7.411 | —0.301 |
| 0.200 | 7.35 | 2.10 | 7.678 | —0.699 |
| 0.100 | 7.13 | 1.19 | 7.926 | —1.000 |
| **Potassium Iodide** n** = 1.493 | | | | |
| 1.000 | 9.35 | 9.35 | 7.029 | 0.000 |
| 0.500 | 2.74 | 9.75 | 7.011 | —0.301 |
| 0.200 | 1.11 | 9.15 | 7.039 | —0.699 |
| 0.100 | 1.09 | 3.25 | 7.489 | —1.000 |
| **Sodium Iodide** n** = 1.587 | | | | |
| 1.000 | 9.15 | 9.15 | 7.039 | 0.000 |
| 0.500 | 2.80 | 9.31 | 7.031 | —0.301 |
| 0.200 | 1.13 | 8.83 | 7.054 | —0.699 |
| 0.100 | 1.12 | 2.91 | 7.536 | —1.000 |
| **Sodium Perchlorate** n** = —0.472 | | | | |
| 1.000 | 0.63 | 0.63 | 8.204 | 0.000 |
| 0.500 | 1.16 | 0.84 | 8.076 | —0.301 |
| 0.200 | 2.82 | 1.32 | 7.880 | —0.699 |
| 0.100 | 5.38 | 1.82 | 7.741 | —1.000 |
| **Barium Perchlorate** n** = —0.445 | | | | |
| 1.500 | 0.72 | 0.86 | 8.067 | 0.176 |
| 0.750 | 1.23 | 1.08 | 7.965 | —0.125 |
| 0.300 | 2.98 | 1.74 | 7.759 | —0.523 |
| 0.150 | 5.13 | 2.20 | 7.657 | —0.824 |

* $S_o$ is given in terms of moles Cd x $10^8$ x 100 $ml^{-1}$ x $cm^{-2}$ x $min.^{-1}$.

** n is the order of reaction due to the salt.

of temperature also can be considered to be constant since all experiments were run at 25 ± 0.1 C. The effect of diffusion can be regarded as negligible due to the vigorous agitation of the solution caused by the degassing process and the speed of rotation of the cadmium bar. The effect of the oxygen concentration on the initial dissolution rate may be considered to be constant since carbon dioxide-free air was continually passed through the salt solution at a rate of 75 ml per minute.

The samples of cadmium were made from the same reagent grade material and were prepared in identical ways; thus, the effect of the history and surface characteristics of the cadmium bar were constant. It can be seen then that all variables other than the nature of the salt and the concentration of the salt solution which would effect the initial rate of dissolution of cadmium were constant and thus could be disregarded when studying the effect of the salts and concentrations of the salt solutions.

The data shown in Table 1 indicate that the anion in neutral salt solutions influences the initial rate of dissolution of cadmium much more than does the cation. Salts containing the same anion but different cations were found to have the same, or nearly the same, order of reaction, n, due to salts as calculated from Equation (1). Since the perchlorate salts used in this study gave a negative value for n, it is thought that the cations have an effect on the initial rate of dissolution since, if no other factors were involved, the initial rate should be slower than is indicated. This is because the rate of dissolution of cadmium in carbon dioxide-free, air-saturated water is slower than in neutral solutions of perchlorate salts. If there were no other factors involved other than the influence of the anion, the rate of dissolution in the perchlorate salt solutions should be slower than found in these experiments due to the perchlorate ion acting as an inhibitor to the dissolution process. Hence, it must be assumed that the cations also have an influence on the initial rate of dissolution of cadmium but that this effect is smaller than that due to the anion.

There are many references in the literature[12, 14, 15] to the fact that there are maxima and minima in the corrosion rate versus salt concentration curves. However, the data obtained in these experiments were from rather long corrosion experiments in which factors such as corrosion products would influence the rate of corrosion. These data were not for initial corrosion rates as determined in this work. It is not surprising, though, to find that similar maxima occur for initial corrosion rate versus concentration curves obtained from the data for the iodide salts. Note that the plot of the logarithm of the ionic strength versus the logarithm of the initial dissolution rate for both potassium and sodium iodides indicate a maxima in the same region of concentration for both salts (see Figure 3). It can be seen also that the curves shown in Figures 1, 2, and 4 are very similar for salts containing a common anion, which helps support the view that the anion has a much greater effect on the initial dissolution rate than does the cation.

The negative order of reaction due to the perchlorate salts indicates that the perchlorate ion inhibits the initial rate of dissolution of cadmium. It is thought that the perchlorate ion forms a film on the surface of the cadmium and thus inhibits the dissolution process. The film of perchlorate ions is considered to be a chemisorbed film in distinction to the physically bound protective layers of corrosion products which are formed during the latter stages of corrosion.[16, 17, 18]

The values of K for the various concentrations of salt solutions calculated from Equation (1) are tabulated in Table 1. The values of K for perchlorate salts help support the view that the perchlorate ion acts as an inhibitor in the initial corrosion rate due to its being adsorbed on the surface of the cadmium metal; this effect has been called anion polarization. If it is assumed that as the concentration of perchlorate ion increases, the greater is the amount of surface of the cadmium metal protected by the perchlorate ion, then the effective area of the cadmium bar exposed to the solution also would decrease. Thus, the value observed for $S_o$, the initial rate of dissolution, is lower than the true value based on the true exposed area of cadmium.

It is seen in Figure 3 that the initial rate of dissolution, $S_o$, for the iodide salts in the range of ionic strength of 0.5 to 1.0 is similar in many respects to the initial rate of dissolution for the perchlorate salts over the whole range of ionic strength investigated. Thus, it might be expected that at the higher concentration of iodide salt, a film of iodide ions forms on the cadmium bar. It also might be expected that the rate of film growth with concentration of iodide salt is not as great as that with the perchlorate salts. Hence, up to an ionic strength of about 0.5, the anion polarization due to iodide ions is not sufficiently great to influence the results obtained here within experimental error. Therefore, the abnormalities of the initial rate of dissolution of cadmium in neutral salt solutions observed can be attributed to anion polarization of the surface of the cadmium metal.

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# Saturable Reactors For Control Rectifiers★

BY HARRY E. KROON*

**Abstract**

Electrolysis studies indicated that inadequate drainage of a one-mile long 350,000 circular mil drain wire had created cable-to-earth potentials ranging from + .15 to + .35 volt in certain areas. This situation was corrected through the use of a magnetic amplifier used to vary the rectifier output simultaneously with the erratic positive cable-to-earth potentials. Experience to date indicates this controlled magnetic amplifier not only performs effectively but also requires a minimum of maintenance. 5.2.3

ELECTROLYSIS STUDIES made in the Oak Park district indicated that there was a need for increased drainage in the existing one mile long 350,000 circular mil drain wire from the River Forest area to the Des Plaines Street sub-station, Harrison and Des Plaines Streets, Forest Park, Illinois.

The inadequate drainage created positive cable to earth potentials ranging from .15 to .25 volt in the River Forest area and in portions of the Oak Park and Maywood area. This condition existed for about 20 hours of the 24-hour cycle. During the heaviest load times, from 6 am to 8 am and 5 pm to 7 pm, the condition became worse. The cable to earth potentials were more erratic during these times, and the magnitude varied from plus .25 to plus .35 volt.

A study of various arrangements indicated that a magnetic amplifier in the drainage wire circuit would provide the most economical solution to the problem. This system would permit the drainage current to be controlled so that other underground metallic structures in this urban area would not be unduly affected.

Preliminary tests were made with the cooperation of owners of other subsurface structures, and they indicated no objection to the installation of a controlled magnetic amplifier in the drainage system. Arrangements were made with the Vickers Electric Division of St. Louis, Missouri, to provide a 60 ampere, 28 volt magnetic amplifier to operate from a 220 volt 3 phase 60 cycle power supply. The current output of this amplifier would be controlled by the the existing currents trying to return from the cables to the Des Plaines Street sub-station.

This controlled magnetic amplifier, the first of its kind in the Illinois Bell System, was installed along the Northwestern right-of-way on Central Street and east of the Soo Line Railroad, River Forest. The unit was placed in operation on May 14, 1956.

Current surveys indicate the approximate area cleared of unsatisfactory conditions included cables in Oak Park, River Forest and Maywood. A satisfactory negative cable to earth potential margin of 0.1 to 0.2 of a volt was created.

### Operation of Magnetic Amplifier

The magnetic amplifier in this drainage wire circuit is a single stage amplifier and operates in the following manner:

The amplifier system (Figure 1) includes a three phase power transformer, a three phase selenium rectifier for converting alternating current to direct current, a saturable reactor in each phase wire between the power transformer and the selenium rectifier, and a source of bias current.

Each saturable reactor has three control windings and an output winding. The corresponding numbered control winding of each reactor is connected in series. The bias current acting in each of the series connected control windings of the three reactors sets the minimum output current of the amplifier and this determines the minimum negative cable to earth potential. The natural currents returning to the sub-station over the drainage wire flow through the output windings of the reactors. These currents trigger the reactor circuits resulting in saturation of the reactor cores and a reduction in circuit reactance. This permits the power transformer to deliver increased current to the selenium rectifier and increase the dc output current. The reactance of the circuit is reset each half cycle of power supply frequency to the value determined by the bias current flowing through the bias winding.

The output current may be increased by allowing a portion of the current returning from the cable to the sub-station to flow through one of the other unused control windings in such a direction as to increase the saturation in the reactor cores. The output current may be limited by allowing a portion of the output current to flow through one of the other unused control windings in such a direction as to limit the degree of saturation in the reactor cores. This is called negative feedback. The magnitude of the feedback current can be retarded by the use of a non-linear resistance until the output current reaches its higher values, thus having little effect on the lower values of drainage current.

Experience to date indicates this controlled magnetic amplifier not only performs effectively but also requires a minimum of maintenance.

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* Staff Supervisor, Illinois Bell Telephone Company, Chicago, Illinois.

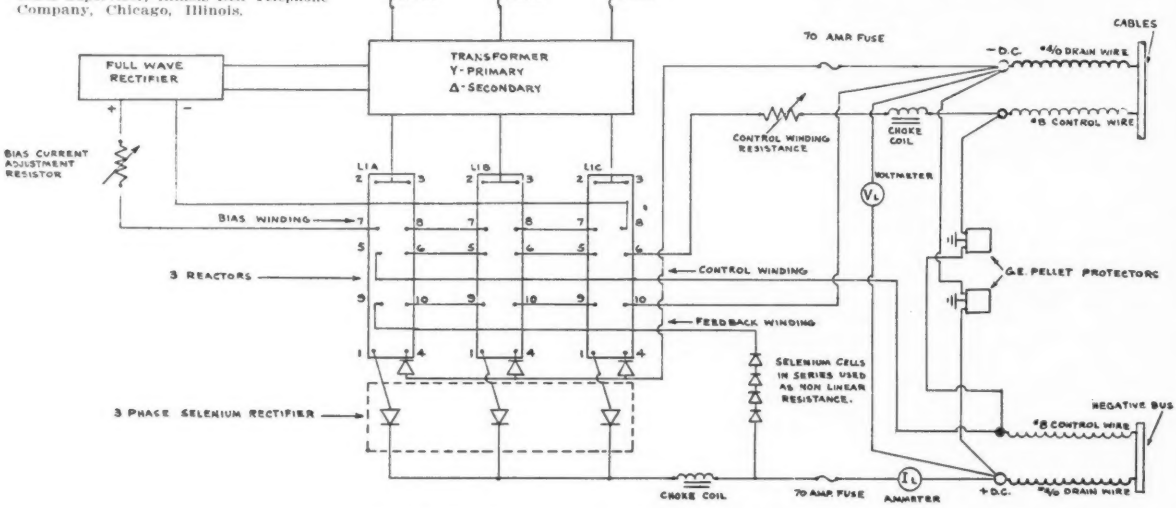



Figure 1—Controlled magnetic amplifier schematic diagram.

Publication 58-13

# SYMPOSIUM ON CORROSION BY HIGH PURITY WATER

*A Contribution to the Work of NACE Technical Committee T-3F On Corrosion By High Purity Water*


Page

The Corrosion Behavior of Zirconium-Uranium Alloys In High-Temperature Water
*By Warren E. Berry and Robert S. Peoples* ..... 34

Corrosion and Water Purity Control For the Army Package Power Reactor
*By Richard J. Clark and A. Louis Medin* ..... 39

Removal of Corrosion Products From High Temperature, High Purity Water Systems With an Axial Bed Filter
*By R. E. Larson and S. L. Williams* ..... 44

Some Relations Between Deposition and Corrosion Contamination in Low Make-Up Systems For Steam Power Plants
*By E. S. Johnson and H. Kehmna* ..... 49
Discussion: Robert D. Misch, Page 53; B. A. Kronmiller, Page 53; W. A. Keilbaugh, Pages 53 and 54; Replies by E. S. Johnson and H. Kehmna, Page 54.


NOTE: All of the above listed papers were presented at the High Purity Water Symposium at the Fourteenth Annual Conference, National Association of Corrosion Engineers, San Francisco, California, March 17-21, 1958

# The Corrosion Behavior of Zirconium-Uranium Alloys In High-Temperature Water

By WARREN E. BERRY* and ROBERT S. PEOPLES*


## Abstract

The effect on corrosion behavior of water temperature, uranium content, and oxygen content has been determined for zirconium 7 through 70 weight percent uranium alloys. Corrosion rates increased as water temperature increased from 500 to 680 F, as uranium alloy content increased, and in general as oxygen content in the alloys increased. The amount and distribution of epsilon phase present in alloys containing up through 55 weight percent uranium determined their corrosion behavior. The amount of alpha uranium controls the corrosion behavior of alloys containing more than 60 weight percent uranium. Increase in corrosion rates with increasing oxygen in alloys in the epsilon composition range of 45 to 55 weight percent uranium can be correlated with the effect of oxygen on the stability of the epsilon phase. Microstructures reveal an increase of a second phase (alpha zirconium) with increasing oxygen content. 6.3.20


## Introduction

THE LOW thermal-neutron-absorption cross section of zirconium makes it an attractive alloying agent for uranium fuels in nuclear reactor applications. Alloys containing up to 60 weight percent uranium are easily fabricated, bond well to Zircaloy cladding, and possess reasonably good corrosion resistance in high-temperature water.[1]

In water-cooled reactor applications, the fuel is clad with a corrosion-resistant envelope such as zirconium, not only to ensure that the core does not corrode but also to prevent fission products from entering the cooling stream. However, since the envelope might develop a leak and allow water to reach the core, it is necessary to know the corrosion behavior of the potential fuel alloy.

The use of zirconium alloys containing up to 60 weight percent uranium as a reactor fuel has been considered and there is information available on the corrosion resistance of several of these alloys in high-temperature water.[2,3,4,5] In addition, several surveys have been conducted on the corrosion behavior of zirconium-base uranium alloy series covering a wide composition range.[6,7,8] Recent work has resulted in a better understanding of the uranium-zirconium alloy system. It has been shown that the intermediate epsilon phase exists over the range of 45 to 53 weight percent uranium and that decomposition of epsilon occurs with oxygen additions.[9]

Taking the above background information into consideration, a program was undertaken to determine the effect of water temperature and oxygen content in the zirconium melting stock on the corrosion behavior of zirconium base 7 through 70 weight percent uranium alloys. The information thus obtained would be useful in engineering future reactors.

Cracking and premature failures have been reported for corrosion-tested alloys which were quenched from the beta phase[1,5,6] (solid solution of beta zirconium and gamma uranium). These failures probably were due to a type of stress-corrosion cracking, since it has been reported that partial transformation of beta in 20 through 80 weight percent uranium alloys results in a marked hardness increase which could provide internal stress.[10] Beta may transform at the corrosion test temperature or it may be partially transformed as a result of quenching conditions.[11] To avoid this effect, all alloys in the present study were corrosion tested in the equilibrium condition (i.e., alpha zirconium plus epsilon for zirconium-rich alloys, epsilon for 45 to 55 weight percent uranium alloys, and epsilon plus alpha uranium for uranium-rich alloys).

## Experimental

### *Test Procedures*

Alloys were double melted from biscuit uranium and several grades of zirconium by consumable electrode arc-melting techniques. Zirconium melting stocks were crystal bar, sponge, and high-oxygen sponge (alloyed with oxygen) with oxygen contents of approximately 0.005, 0.10, and 0.30 weight percent, respectively. Spot-check analyses revealed that alloys containing less than 20 weight percent uranium varied less than 0.5 weight percent from intended composition, and alloys containing more than 20 weight percent uranium did not vary more than 2 weight percent from the intended composition. Alloys were rolled to sheet at 790 to 840 C.

**Heat Treatment.** The hot-rolled sheet from each alloy was heat treated to produce the equilibrium phases and avoid undue brittleness in the alloys. Samples were first shaper finished to remove surface contamination. They were then inserted in vycor capsules which were evacuated to a pressure of 0.1 micron of mercury. The capsules were left open to the pumps and were heated to 800 C. After 1 hour at 800 C, the capsules were cooled at a rate of 100 C per hour to 500 C. The power was then turned off and the capsules allowed to cool in the furnace.

**Preparation of Samples.** Any light tarnish film on heat-treated samples was removed by taking a light shaper cut. Final dimensions of the test samples were approximately 1.00 x 0.50 x 0.10 inches. Samples were measured, degreased, and weighed. After each exposure period, loosely adherent corrosion product was removed by brushing prior to weighing.

**Autoclave Testing.** Corrosion tests were conducted in 1-liter Type 316 stainless steel autoclaves. Samples were supported in individual Chromel A wire baskets which were in electrical contact

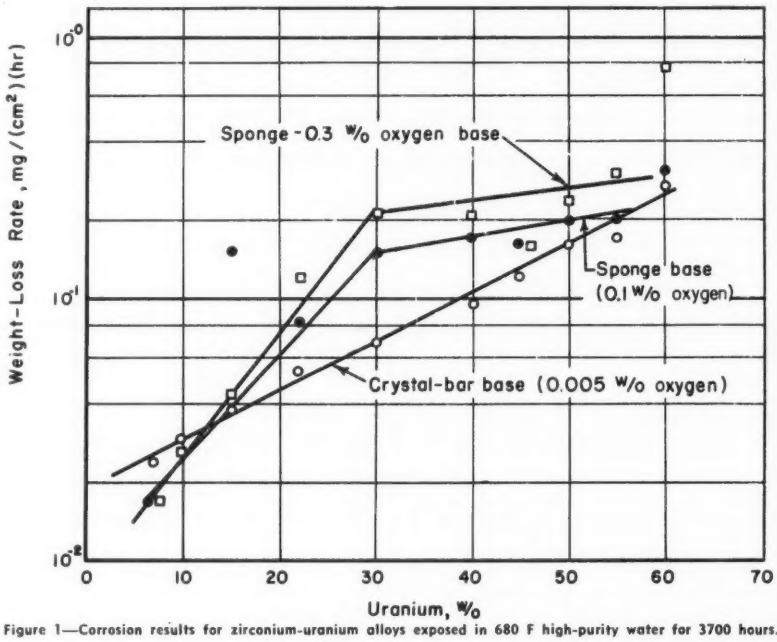



Figure 1—Corrosion results for zirconium-uranium alloys exposed in 680 F high-purity water for 3700 hours.

* Battelle Memorial Institute, Columbus, Ohio.

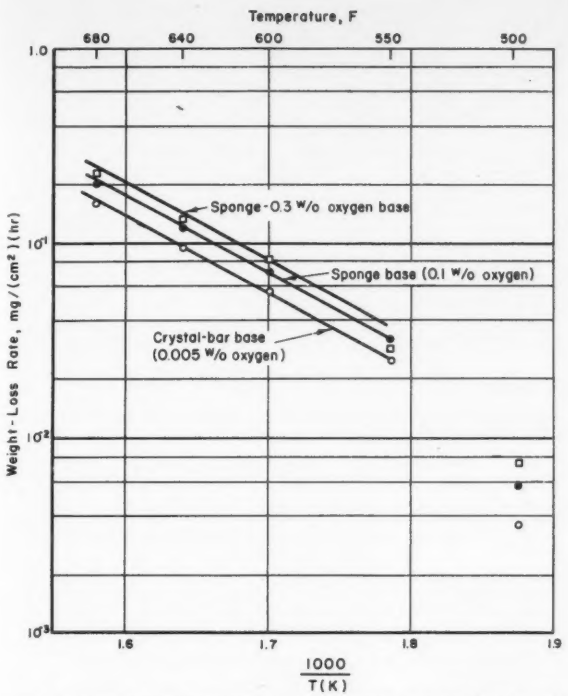



Figure 2—Temperature dependency of the corrrosion rate of zirconium—50 weight percent uranium alloys in high-temperature water.

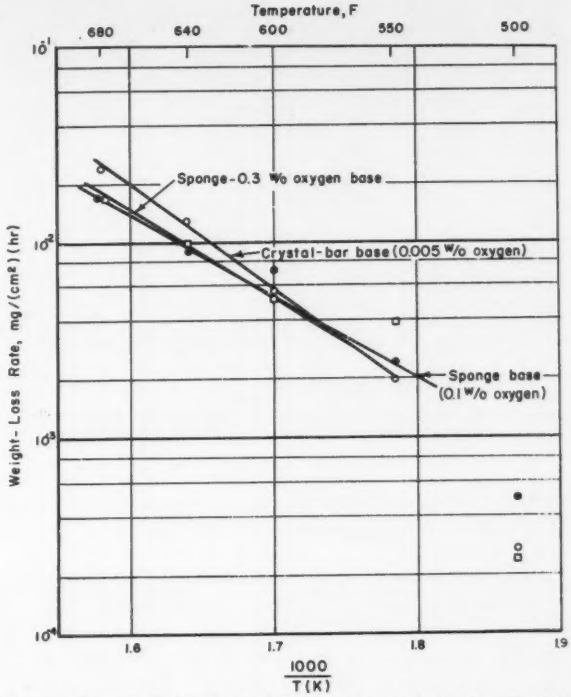
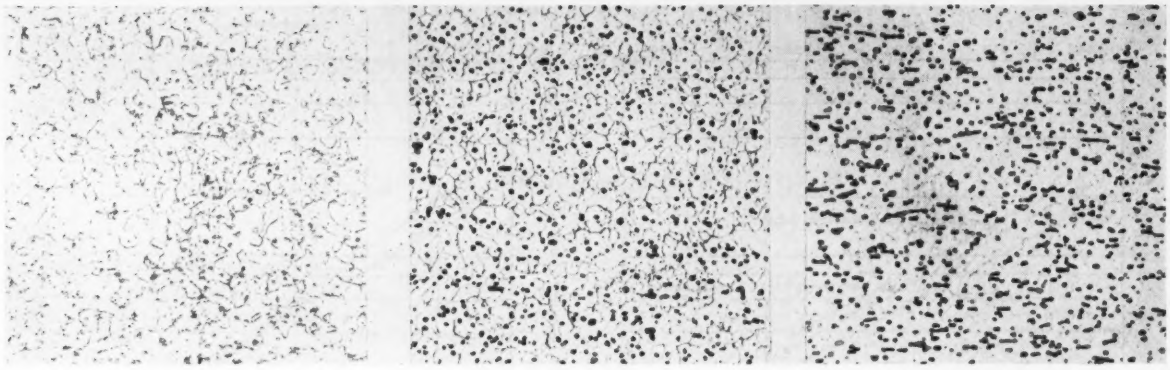



Figure 3—Temperature dependency of the corrosion rate of zirconium—7 weight percent uranium alloys in high-temperature water.

**TABLE 1—Corrosion Results Obtained for Zirconium-Uranium Alloys Exposed in High-Temperature High-Purity Water**

| Nominal Uranium Content (Balance Zirconium), Weight Percent | Zirconium Melting Stock | WEIGHT-LOSS RATE, mg/(cm²) (hr), IN WATER AT TEMPERATURE INDICATED | | | | |
|---|---|---|---|---|---|---|
| | | 500 F[a] | 550 F[b] | 600 F[c] | 640 F[b] | 680 F[c] |
| 7 | Crystal Bar | 0.00027 | 0.0020 | 0.0056 | 0.013 | 0.024 |
| | Sponge | 0.00050 | 0.0024 | 0.0073 | 0.010 | 0.017 |
| | Sponge—0.3 weight percent oxygen | 0.00024 | 0.0040 | 0.0052 | 0.0091 | 0.017 |
| 10 | Crystal Bar | 0.00026 | 0.0028 | 0.0073 | 0.016 | 0.029 |
| | Sponge | * | * | * | * | * |
| | Sponge—0.3 weight percent oxygen | 0.00070 | 0.0059 | 0.010 | 0.015 | 0.026 |
| 15 | Crystal Bar | 0.00038 | 0.0039 | 0.010 | 0.018 | 0.037 |
| | Sponge | 0.0031 | 0.025 | 0.059 | 0.097 | 0.15 |
| | Sponge—0.3 weight percent oxygen | 0.0014 | 0.0067 | 0.016 | 0.023 | 0.043 |
| 22 | Crystal Bar | 0.0015 | 0.0064 | 0.019 | 0.033 | 0.052 |
| | Sponge | 0.0049 | 0.010 | 0.032 | 0.052 | 0.082 |
| | Sponge—0.3 weight percent oxygen | 0.0029 | 0.013 | 0.043 | 0.057 | 0.12 |
| 30 | Crystal Bar | 0.0016 | 0.0089 | 0.019 | 0.034 | 0.068 |
| | Sponge | 0.0049 | 0.017 | 0.054 | 0.075 | 0.15 |
| | Sponge—0.3 weight percent oxygen | 0.0051 | 0.027 | 0.063 | 0.11 | 0.21 |
| 40 | Crystal bar | 0.0028 | 0.013 | 0.031 | 0.053 | 0.095 |
| | Sponge | 0.0050 | 0.020 | 0.052 | 0.092 | 0.17 |
| | Sponge—0.3 weight percent oxygen | 0.0050 | 0.027 | 0.063 | 0.12 | 0.21 |
| 45 | Crystal bar | 0.0029 | 0.018 | 0.040 | 0.072 | 0.12 |
| | Sponge | 0.0043 | 0.020 | 0.051 | 0.084 | 0.16 |
| | Sponge—3.0 weight percent oxygen | 0.0044 | 0.021 | 0.055 | 0.091 | 0.16 |
| 50 | Crystal bar | 0.0036 | 0.025 | 0.057 | 0.094 | 0.16 |
| | Sponge | 0.0057 | 0.032 | 0.071 | 0.12 | 0.20 |
| | Sponge—3.0 weight percent oxygen | 0.0075 | 0.029 | 0.083 | 0.13 | 0.23 |
| 55 | Crystal Bar | 0.0069 | 0.032 | 0.068 | 0.10 | 0.17 |
| | Sponge | 0.0064 | 0.034 | 0.075 | 0.12 | 0.20 |
| | Sponge—3.0 weight percent oxygen | 0.0091 | 0.042 | 0.093 | 0.15 | 0.30 |
| 60 | Crystal bar | 0.0065 | 0.031 | 0.069 | 0.12 | 0.27 |
| | Sponge | 0.0082 | 0.039 | 0.082 | 0.15 | 0.31 |
| | Sponge—3.0 weight percent oxygen | 0.017 | 0.069 | 0.20 | 0.34 | 0.77 |
| 70 | Crystal bar | 0.35 | [d] | [d] | [d] | [d] |
| | Sponge | 0.85 | [d] | [d] | [d] | [d] |
| | Sponge—3.0 weight percent oxygen | 1.23 | [d] | [d] | [d] | [d] |

[a] Based on exposure times to 7000 hours.
[b] Based on exposure times to 2350 hours.
[c] Based on exposure times to 3700 hours.
[d] Completely oxidized after 168-hour exposure.
* No alloy.



Crystal-Bar Base (0.005 Weight Percent Oxygen)

Sponge Base (0.10 Weight Percent Oxygen)

Sponge—0.3 Weight Percent Oxygen Base

Figure 4—Photomicrograph of zirconium—50 weight percent uranium alloys. Note increasing amount of precipitated alpha zirconium with increasing oxygen content in zirconium melting stock. Original magnifications, 500X; actual magnifications after reduction for engraving purposes, 375X.

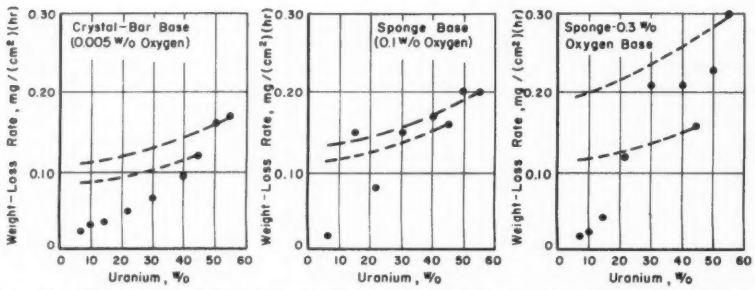



Figure 5—Corrosion results obtained with zirconium-uranium alloys in 680 F high-purity water. Dotted lines define limits of corrosion rates which would be obtained if epsilon were the matix phase.

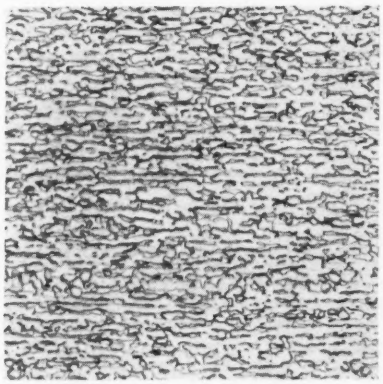
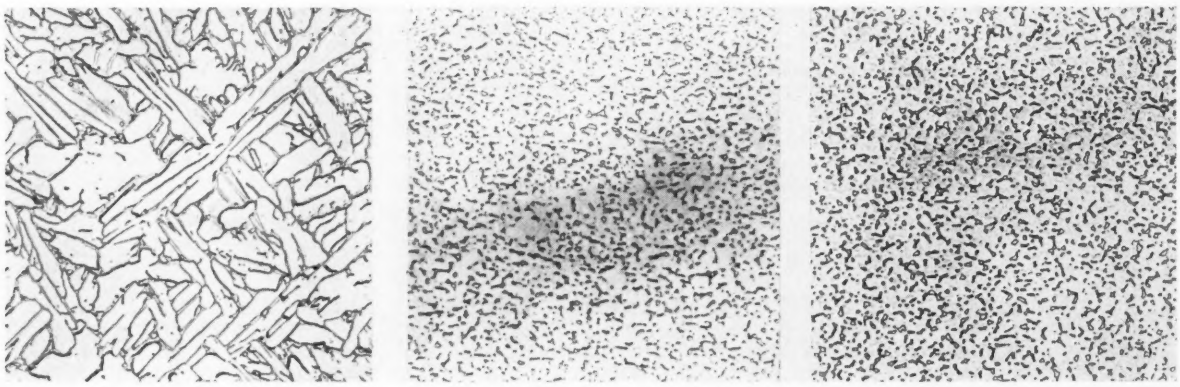


Figure 6—Photomicrograph of sponge zirconium-base 15 weight percent uranium alloy. Note the almost continuous epsilon phase. 500X.



Crystal-Bar Base (0.005 Weight Percent Oxygen)

Sponge Base (0.10 Weight Percent Oxygen)

Sponge—0.3 Weight Percent Oxygen Base

Figure 7—Photomicrographs of zirconium—7 weight percent uranium alloys. Alpha zirconium matrix and epsilon.

with the autoclave. Test water of 1 megohm specific resistivity was boiled one hour to remove dissolved gases. The boiling water was then transferred to the autoclave which was quickly sealed. The autoclave was heated and a measured amount of water bled off to purge the fittings of air and to ensure a 10 percent headspace at temperature. Fresh water was added after each 7-day-exposure period.

*Test Results*

The corrosion behavior of zirconium-uranium alloys in water was studied at 5 test temperatures: 500, 550, 600, 640, and 680 F (260, 288, 315, 338, and 360 C, respectively). Alloy compositions included 7, 10, 15, 22, 30, 40, 45, 50, 55, 60, and 70 weight percent uranium additions to crystal bar, sponge, and high-oxygen (0.3 weight percent) zirconium.

In general, loosely adherent corrosion products formed on test samples and they lost weight at a linear rate. Exceptions were the 22 weight percent uranium-sponge and high-oxygen sponge-base alloys which alternately gained and lost weight at irregular intervals, thus indicating the formation and subsequent spalling of the corrosion film. Alloys containing 70 weight percent uranium were completely oxidized after 168 hours in 550, 600, 640, and 680 F water, but survived at least 672 hours in 500 F water.

Corrosion rates for the alloy series at each water temperature are presented in Table 1. Results are based on exposure times ranging from 2350 to 7000 hours. Changes in area due to metal loss from corrosion were taken into consideration in calculating the corrosion rates. Ad-

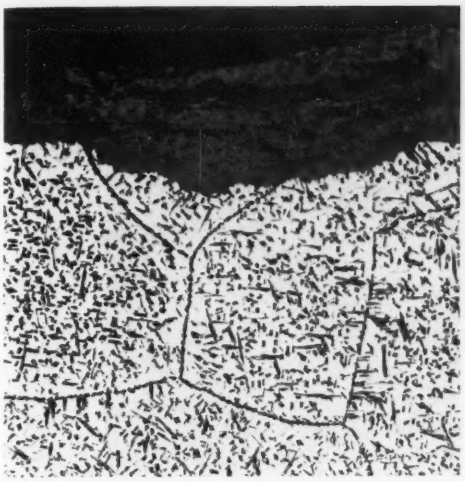



Figure 8—Photomicrograph of crystal-bar zirconium—30 weight percent uranium alloy exposed 3700 hours in 680 F water. Note alpha zirconium at grain boundaries which apparently retards penetration. 250X.

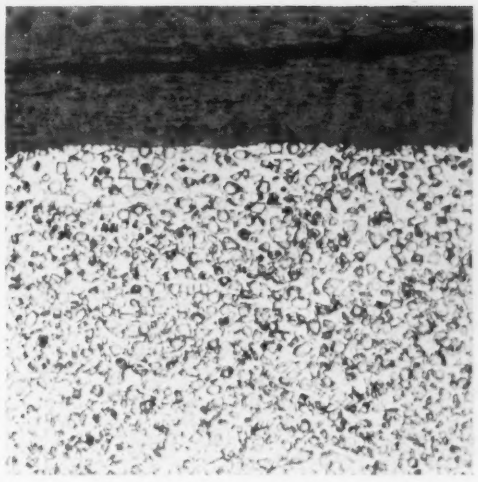
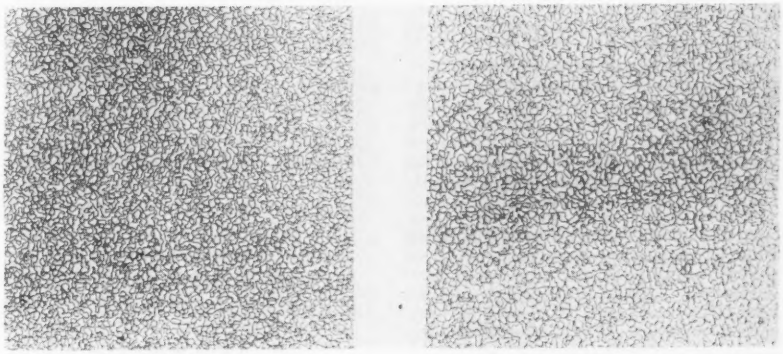



Figure 9—Photomicrograph of sponge zirconium—30 weight percent uranium alloy exposed 3700 hours in 680 F water. Note random dispersion of alpha zirconium in epsilon and uniform attack at surface. 250X.



Sponge Base (0.10 Weight Percent Oxygen)

Sponge—0.3 Weight Percent Oxygen Base

Figure 10—Photomicrographs of zirconium—22 weight percent uranium alloys. Note finely divided structure of alpha zirconium and epsilon. Oirginal magnification, 500X; actual magnification after reduction for engraving purposes, 360X.

herent oxide on the 22 weight percent uranium alloys was mechanically removed and an average corrosion rate calculated based on the total weight loss and total exposure time. The plot of alloy content versus corrosion rate in 680 F water in Figure 1 is typical for results at all temperatures. It is apparent from the curves that, in general, the corrosion rates increased with increasing uranium content. The increase was uniform for crystal-bar zirconium-base alloys. However, corrosion rates of sponge and high-oxygen sponge-base alloys increased sharply as uranium content increased to about 30 weight percent. Above 30 weight percent uranium, the increase in rates was less pronounced.

The effect of oxygen on corrosion behavior is also shown in Figure 1. At low uranium levels, oxygen in the zirconium melting stock appeared to have no adverse effect on corrosion behavior. However, for any alloy above 22 weight percent uranium, the corrosion rate increased with increasing oxygen content.

The effect of temperature on corrosion behavior of the epsilon phase 50 weight percent uranium alloy is shown in Figure 2. Values for 500 F water exposure did not fall on the plotted curve, indicating the possibility of a change in reaction mechanism at this temperature. No attempt was made to investigate this change in mechanism. Although the corrosion rates varied with oxygen content of the zirconium, the slope of the temperature dependency plot was the same for each zirconium melting stock. Temperature-depending plots of essentially the same slope were obtained for all alloys containing 22 to 60 weight percent uranium. In crystal-bar base alloys containing up to 15 weight percent uranium, the slope of the temperature dependency plot was steeper than those for the sponge or high-oxygen sponge-base alloys. This effect is shown for 7 weight percent uranium alloys in Figure 3.

*Discussion*

The corrosion behavior of these zirconium-uranium alloys can be explained on the basis of the equilibrium phases present in the alloys. Alloys containing 45 to 55 weight percent uranium should corrode as single-phase epsilon unless there is sufficient oxygen in the alloys to cause the formation of alpha zirconium and alpha uranium in the structures. Alloys of less than 45 weight percent uranium contain alpha zirconium and epsilon, and the amount and distribution of the two phases should determine corrosion behavior. Alloys with more than 55 weight percent uranium contain alpha uranium and epsilon (plus alpha zirconium at high-oxygen levels), and the amount and distribution of these two phases should control corrosion behavior.

**Epsilon-Phase Alloys.** Zirconium alloys containing approximately 45 to 55 weight percent uranium should be single-phase epsilon. However, the presence of up to 0.3 weight percent oxygen in these alloys affects the range of the epsilon phase and results in the formation of some alpha zirconium and alpha uranium in the 55 weight percent alloys and the formation of alpha zirconium and uranium enrichment of the epsilon in the 45 and 50 weight percent alloys.[12] Increased corrosion rates with increasing oxygen content can be attributed to uranium enrichment of the epsilon phase in 45 and 50 weight percent alloys, and to the presence of alpha uranium in 55 weight percent uranium alloys. The effects of oxygen in increasing the amount of alpha zirconium in the microstructure is evident in the photomicrographs of 50 weight percent uranium alloys presented in Figure 4.

**Alloys Containing Alpha Zirconium Plus Epsilon.** Alloys with less than 45 weight uranium contain epsilon plus alpha zirconium. At approximately 30 weight percent uranium, the equilibrium volume percentages of the two phases are equal. Alpha zirconium is the predominant phase below 30 weight percent uranium and epsilon is the predominant phase above 30 weight percent uranium (at low-oxygen levels). Dispersion of the two phases in the microstructure could play an important role in determining corrosion behavior, since alpha zirconium is much more corrosion resistant than epsilon. For example, if it is assumed that, in the alloys studied, epsilon is the matrix and completely surrounds the alpha zirconium, weight-loss rates can be calculated based on the rate of penetration of the epsilon phase and the density of each alloy. Corrosion rates should fall within limits, as calculated from the corrosion rates of epsilon of 45 weight percent and 55 weight percent uranium composition. Figure 5 is

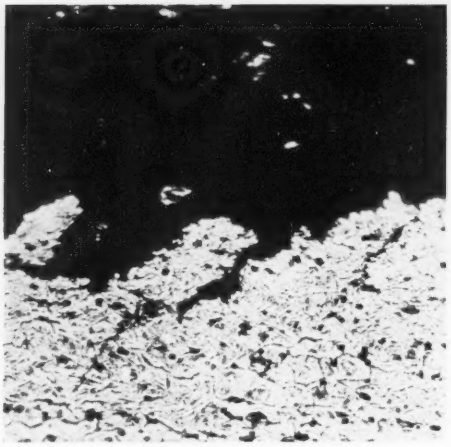



Figure 11—Photomicrograph of sponge zirconium—70 weight percent uranium alloy exposed 1176 hours in water at 500 F. Note needles of alpha uranium and selective attack dislodging pieces of unoxidized metal. Original magnification, 500X; actual magnification after reduction for engraving purposes, 440X.

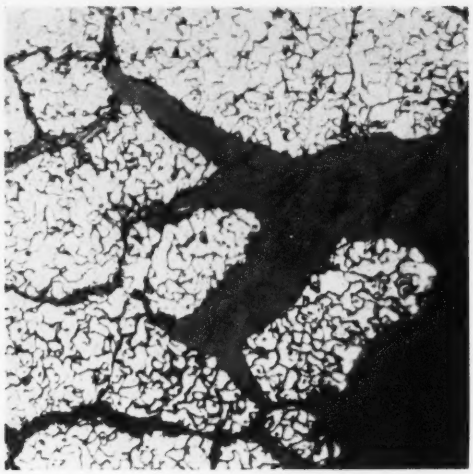



Figure 12—Photomicrograph of crystal-bar zirconium base—60 weight percent uranium sample exposed 1850 hours in 680 F high-purity water. Note attack in alpha uranium at grain boundaries. Original magnification, 500X; actual magnification after reduction for engraving purposes, 440X.

a plot of these limits and observed corrosion rates in 680 F water. Results at other temperatures are similar. It can be seen that, with crystal-bar-base alloys, only the rates for the 45 to 55 weight percent alloys fall within the limits, whereas the rates for all sponge and high-oxygen sponge-base alloys above 30 weight percent uranium fall within the limits. The corrosion rate for the sponge base 15 weight percent uranium alloy also falls within these limits. Close examination of the microstructure of this alloy presented in Figure 6 reveals that the laminar alpha zirconium appears to be completely surrounded by epsilon, thus accounting for its abnormally high corrosion rate.

In alloys containing less than 30 weight percent uranium, alpha zirconium occupies the larger volume and apparently is sufficiently continuous to retard corrosion. Photomicrographs of 7 weight percent uranium alloys in Figure 7 show the presence of epsilon in an alpha zirconium matrix. With increasing uranium, the amount of epsilon phase increases and, hence, the corrosion rates increase. Above 30 weight percent uranium epsilon should be the matrix phase. However, the crystal-bar-base alloys above 30 weight percent uranium contained alpha zirconium at the grain boundaries and in the form of needles which apparently offered some resistance to attack. This is illustrated in the photomicrograph of a corrosion-tested crystal-bar base—30 weight percent uranium alloy in Figure 8. It can be seen that attack is penetrating into the body of the grain, but is retarded along the grain boundaries. This type of attack resulted in a roughened surface on the 30 and 40 weight percent uranium-crystal-bar base alloys. On the other hand, alpha zirconium was randomly distributed in an epsilon matrix in 30 and 40 weight percent uranium-sponge and sponge-oxygen-base alloys. The attack on these samples was more uniform and apparently occurred in the epsilon and bypassed the alpha zirconium. A photomicrograph of a corrosion-tested sponge base—30 weight percent uranium alloy is presented in Figure 9.

In Figure 10 are photomicrographs of the sponge and high-oxygen sponge base—22 weight percent uranium alloys which alternately gained and lost weight. The finely divided microstructure of these alloys may be responsible for the growth of an adherent film which subsequently breaks up and spalls.

**Alloys Containing Alpha Uranium Plus Epsilon.** Zirconium alloys of more than 55 weight percent uranium content consist of epsilon plus alpha uranium and alpha zirconium, if oxygen is present in the alloy. The high-temperature water corrosion resistance of alpha uranium is extremely poor with a reported weight loss in excess of 6000 mg/(cm$^2$) (hr) at 600 F.[13] Since epsilon corrodes at a rate of —0.2 mg/(cm$^2$) (hr) in 680 F water, it is obvious that the amount and distribution of alpha uranium in the microstructure would control corrosion behavior. The quantity of alpha uranium in the 70 weight percent alloys accounts for their rapid failure in water above 550 F. The nature of the attack is shown in Figure 11 which shows a photomicrograph of a sponge base—70 weight percent uranium alloy exposed 1176 hours in 500 F water. The corrosion process has encircled and isolated areas of epsilon which are then dislodged from the surface. Attack in the 60 weight percent alloys occurred preferentially in the alpha uranium at the grain boundaries as shown in Figure 12.

## Conclusions

1. The corrosion rate in high-temperature water of annealed and furnace-cooled zirconium uranium alloys increases with increasing water temperature, increasing uranium content, and increasing oxygen content.

2. The corrosion rate of annealed and furnace-cooled alloys containing up to 55 weight percent uranium is dependent upon the amount and distribution of epsilon phase in the alloy. The amount of alpha uranium controls the corrosion behavior of alloys containing more than 60 weight percent uranium.

3. Increase in corrosion rates with increasing oxygen in alloys in the epsilon composition range of 45 to 55 weight percent can be correlated with the effect of oxygen on the stability of the epsilon phase. Microstructures reveal an increase of a second phase (alpha zirconium) with increasing oxygen content.

## Acknowledgment

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# Corrosion and Water Purity Control For the Army Package Power Reactor

By RICHARD J. CLARK* and A. LOUIS MEDIN**


## Abstract

The Army Package Power Reactor is a 10 MW heat rated system designed to produce 2000 KW of electricity. The reactor, which has been in operation since April, 1957, is a pressurized water system. Problems facing the designer of such a system in the fields of corrosion and water purification are presented. A complete description of the primary purification system is included, along with performance data on individual components. The 2 cubic foot demineralizer has performed very satisfactorily, consistently maintaining coolant resistivity above 600,000 ohm cm. Primary coolant pH generally has averaged about 7.5-8.5, depending on the amount of in-leakage into the primary system. Operation of the purification system has required only minimal attention with even hydrogen control being self-regulating. The experimental in-plant equipment for determining crude levels, corrosion rates, and other related parameters, are described. Although still preliminary, it appears that the corrosion rate of system components has been lower than the originally estimated .05 mg/cm²/mo. 8.4.5


## Introduction

THE ARMY Package Power Reactor, usually referred to as the APPR-1 (Figure 1), is located at Port Belvoir, Virginia. It is a nominal 10 MW heat reactor producing about 2000 KW of electricity. The plant, designed, constructed and operated by Alco Products, Inc., is based on an original conceptual design by Oak Ridge National Laboratory. It has been on the line since April, 1957.

Since the APPR-1 is a pressurized water reactor, high purity water is used both as coolant and moderator. As shown in Figure 2, 1200 psi water circulates through the fully enriched $UO^2$-SS core at the rate of 4000 gpm. During this process the water is heated to 450 F and then passes through a vertical U-tube steam generator. By the exchange of this heat to the secondary system the coolant temperature is reduced to approximately 430 F before being returned to the reactor. A by-pass purification system containing two ion exchangers and a filter is used to prepare and maintain water purity.

The major material of construction for all components in the primary system is AISI Type 304 stainless steel. Unlike other pressurized water reactors which are presently in operation, even the fuel elements are clad and alloyed with Type 304L stainless. Minor materials of construction include stellite, 17-4 PH, Type 410 stainless, Haynes-25 alloy, etc.

## Design Considerations

One of the advantages of water as a reactor coolant is that the radioactive species formed by the interaction of neutrons and oxygen are short-lived (e.g., $O^{16}(n\text{-}p)N^{16}$). Were it not for the presence of radioactive corrosion products in the coolant stream, water would not present a radioactivity problem for any length of time after shutdown.

The effect of radiation introduces a parameter upon water chemistry which is foreign to conventional systems. Radiation promotes some chemical reactions of great importance. It may simplify corrosion control, as will be shown for the case of oxygen removal or it may promote the formation of objectionable substances, such as acids which aggravate the corrosion problem. Maintaining an alkaline pH or use of a corrosion inhibitor is influenced by considerations of induced radioactivity, radiation decomposition or nuclear reactions, as well as thermal stability.

The corrosion problem in the APPR-1 primarily resolves itself into the reaction of stainless steel with high purity water at elevated temperatures. Much effort has been expended over the past eight years in determining the behavior of stainless under these conditions. The relative importance of some of the variables affecting the corrosion rate of this material will be discussed, along with the results of efforts at controlling these variables in the APPR-1.

## Purification System Design

In conventional power and utility plants the purity of the boiler water is controlled by a continuous schedule of blowdown and makeup. The same principle was followed in design of the purification system for the APPR-1. A small portion of water is continuously withdrawn from the main primary system, purified by mixed bed demineralizers, and reintroduced as makeup.

As shown in Figure 2, primary coolant enters the purification system at approximately 430 F and 1200 psi. The temperature is reduced to about 100 F in a heat exchanger to protect the demineralizer resins from thermal damage. A motor-operated throttling valve reduces the pressure to less than 100 psi before the water passes through one of two mixed bed demineralizers. Demineralizer influent also includes a small amount of control rod seal leakage water, and as required, make-up condensate to replace sampling losses. A porous stainless steel filter downstream of the demineralizers serves to collect any resin fines leached from the bed.

The purified water is collected and stored in a 5000 gallon stainless steel tank from which it is recirculated to the primary system and control rod seals by one of two positive displacement pumps. A hydrogen blanket is maintained over the water in the tank to prevent air in-leakage and to introduce sufficient hydrogen into the water to suppress dissociation of the coolant. Regulating valves are set to maintain a hydrogen concentration of 28-30 cc/kg in the coolant.

The make-up tank is different from normal storage tanks in another respect. By extending the inlet pipe well into the center of the tank and enclosing this with a retention chamber, influent water is held-up at least eight hours before mixing with the bulk of water in the tank. Having the delaying chambers in the center utilize the main body of water for shielding in case activity leaches through the demineralizers.

A low pressure hydrogen blanket also

Figure 1—Photograph of Army Package Power Reactor No. 1.

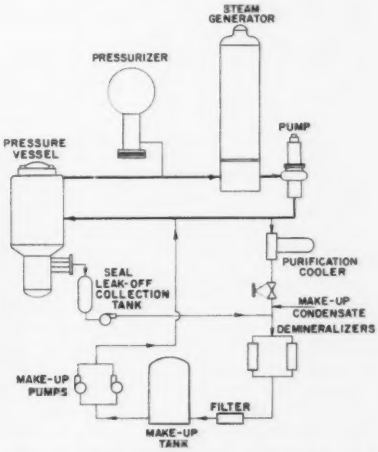


Figure 2—Simplified flow diagram of APPR-1 primary system.

* Head, Chemical Engineering Section, Atomic Energy Engineering, Alco Products, Inc., Schenectady, N. Y.

** Formerly Head, Nuclear Chemical Technology, Atomic Energy Engineering, Alco Products, Inc., Schenectady, N. Y. Now with U. S. Steel Corp., Pittsburgh, Pa.

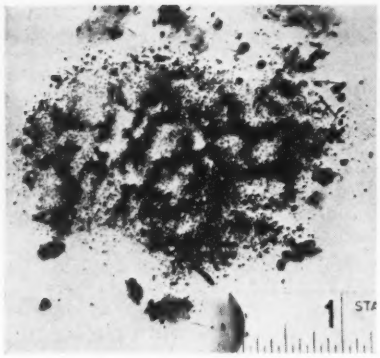

Figure 3—Filter pickup during APPR-1 in-place cleaning.

is maintained over the seal leakoff collection tank to exclude air. Due to design restrictions, the blanket pressure is maintained within the narrow range of 2 to 5 psi.

## Precritical Operation

To ensure cleanliness and the absence of any dirt, oil, metal chips, or weld splatter, special treatment was given all primary system components throughout manufacture, assembly, shipment, and installation. Particular attention was directed at thoroughly degreasing all equipment; even during installation, ultraviolet and other techniques were used to check this point. Since the latter checks disclosed no evidence of oil or grease, in-place chemical treatment was not deemed necessary. However, to remove dust, debris, or loose weld splatter, the primary system was filled with distilled water, and by means of a portable pump, the latter was circulated through a temporary cartridge-type filter. Figure 3 shows a photograph of the weld splatter and other impurities removed on the first run.[1] Although not appreciable, due to the precautions observed during fabrication of the system, the pieces of metal could have caused trouble if not removed. Subsequent runs were made, in which sufficient water to equal several volume changes was passed through new filters, but no additional insolubles were detected.

Before the reactor went critical, a series of non-nuclear tests were performed with dummy fuel elements in the core. Using the pressurizer heaters and an auxiliary boiler feeding steam to the secondary side of the steam generator, the primary system was raised to 1200 psi and 450 F. Since oxygen was present in the initial fill water, and since the initial corrosion film was considered very important, hydrazine was used after filling and venting to remove residual dissolved oxygen. Once the oxygen introduced by filling was eliminated, dissolved oxygen in the coolant was easily held below 0.1 ppm.

The quality of distilled water used for initial fill of the primary system was rather poor, with a specific resistance of about 120,000 ohm-cm and a chloride concentration of about 0.5 ppm. During hydrostatic tests, the efficiency of the purification system was tested, by operating at normal purification rates. Before the completion of the system check-out, resistivity had been raised to 300,000 ohm-cm and chlorides dropped to essentially zero. Demineralizer effluent consistently ran 2 to 4 meg-ohm-cm, and system pH remained relatively constant,[2] in the range of 6.2 to 6.8.

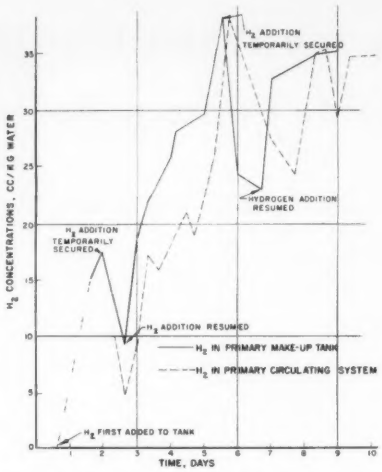


Figure 4—Hydrogen concentration in primary make-up tank and circulating system.

## Plant Start-Up and Operation

At the completion of the dummy core tests, the primary system was drained and refilled with demineralized water. Hydrazine was again added before startup to remove any dissolved oxygen. As the reactor power increased, hydrazine addition was suspended and hydrogen was introduced to the system to maintain zero oxygen residual.

*Hydrogen Control*

Hydrogen control in the system was excellent and easily maintained. Aside from corrosion product hydrogen, the gas was added only to the primary make-up tank, reaching the primary system in the water added as make-up. Figure 4 shows the rapidity with which the hydrogen concentration in the system reached equilibrium with the concentration in the tank. Maintaining an approximate gage reading of 20 to 25 psig from the hydrogen feed tank was adequate to maintain a hydrogen concentration of about 30 cc/kg of water. The effectiveness of the hydrogen was proved in that oxygen has been essentially undetectable during extended plant operation.

*Chloride Control*

The control of chlorides was never a problem. The initial fill water analyzed less than 0.1 ppm, and daily analyses have never exceeded this value.

*Oxygen Control*

Since most of the corrosion products are oxides, dissolved oxygen would be suspected of increasing the corrosion rate. Experience with conventional boiler water systems certainly has shown the necessity of controlling oxygen below 0.05 cc/kg in order to minimize service failures and excessive replacement of parts. Although examination of data obtained from specimens in dynamic loops shows discrepancies, oxygen in the concentrations found in the system apparently does not appreciably affect the corrosion rate of Type 304 stainless steel.[3] Oxygen, however, does have a marked effect on the water chemistry, the corrosion product release rate and localized corrosion, such as pitting and crevice corrosion. The latter is particularly undesirable since it produces large amounts of corrosion product at the mouth of a crevice which, in applications involving moving parts with small clearances, could cause excessive wear or complete seizure.

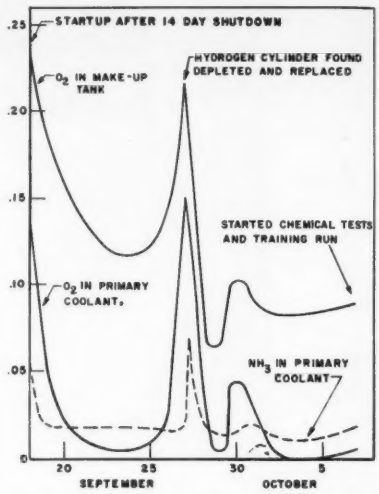


Figure 5—Correlation between $O_2$ and $NH_3$ in primary coolant.

No evidence has resulted to indicate that oxygen is entering the 5000-gallon storage tank. However, the hydrogen blanket pressure of 2-5 psi on the seal leak-off tank has not been completely effective, inasmuch as effluent water from this tank has contained up to 2.5-3.1 ppm of dissolved oxygen. Since the seal leakage water is processed through the demineralizers and returned to the system as part of the make-up water, any oxygen in this water will be introduced into the primary coolant. Because of this in-leakage and/or analytical error, the oxygen content of the make-up water has been approximately 0.01-0.03 ppm. The recombination reaction is so rapid, however, that oxygen has been essentially undetectable during full power operation in the main primary coolant.

Due to radiation synthesis, this in-leakage produces about 0.01 ppm of ammonia in the primary coolant. The latter, in turn, has been partly responsible for the slightly alkaline pH (7.5-8.5) detectable in the primary water.

*pH Control*

High pH (10 to 11) is generally considered to have a beneficial effect in reducing the quantity of corrosion products released in a stainless steel system. Primary coolant pH has generally been about 7.5-8.5 due to ammonia. The ammonia has been attributed to air in-leakage discussed previously, being synthesized from nitrogen and hydrogen by radiation. Figure 5 indicates that a correlation between the oxygen concentration and ammonia formation may exist. Generally, if the oxygen concentration in the coolant is higher than normal, such as at startup or during training and test periods, the ammonia concentration has also increased.

Demineralizer effluent is normally 6.1-6.5. Slightly lower values have been detected on occasion, but this has been attributed to the manner in which pH is measured and the possibilities of carbon dioxide absorption in the open beaker.

An extensive test program is underway to determine the effect of pH on deposition, crud levels, and system activity. However, any data available at this time are too preliminary to indicate the role pH plays in an all-stainless steel system.

*Demineralizer Operation*

The demineralizers have performed very satisfactorily. During the first half year of full power operation, the specific resistance of the primary system consistently has exceeded 600,000 ohm-cm, uncorrected for the presence of hydroxyl ion and ammonia. Resistivity of the ion exchange effluent usually exceeded 2 meg-ohm-cm. Measurements were made with a dip-type cell in an open beaker and the actual resistivity probably was higher than the measured values.

One of the major functions of the demineralizers is to remove radioactive nuclides from the water. Since the resins function both as a filter and an exchanger, the bulk of activity should be removed whether it is present as dissolved or suspended material in the water. Therefore, a valid measure of demineralizer efficiency is the decontamination factor or ratio of radioactivity in the influent to the effluent, both corrected to time of sampling. Efficiencies across the demineralizer were determined by sampling both the influent and effluent at the same time, counting both samples 30 minutes after sampling, and correcting to the instant of sampling.

The mixed bed demineralizers consist of a mixture of strong sulfonic acid type resin in the $H^+$ cycle and a strong basic type resin in the $OH^-$ cycle. Bed depth on the units is 36 inches. Flow loadings generally have been low, even less than 1 gpm/ft² of bed surface.

A single demineralizer has been used for over nine months operating time. The effluent has continuously exceeded 2M ohm-cm resistivity, even when measured with a dip-type cell in an open beaker. As an ion-exchange unit it has functioned very efficiently and according to expectations. As a crud filter, the resin bed also has functioned efficiently, but not entirely as expected. When plotting decontamination factors across the demineralizer, it was envisioned that a straight line parallel to the abscissa would continue until the resin was exhausted, at which time it would drop sharply. This has not been the case. As can be seen in Figure 6, decontamination factors have been decreasing with time.[4]

The top line is the decontamination factors obtained by gross activity counts 30 minutes after sampling. The bottom line was obtained by correcting each sample to the instant of sampling. Each demineralizer effluent sample has had to be corrected by its own decay curve, since these have displayed a non-reproducible decay pattern. There is no apparent explanation for this behavior. Although

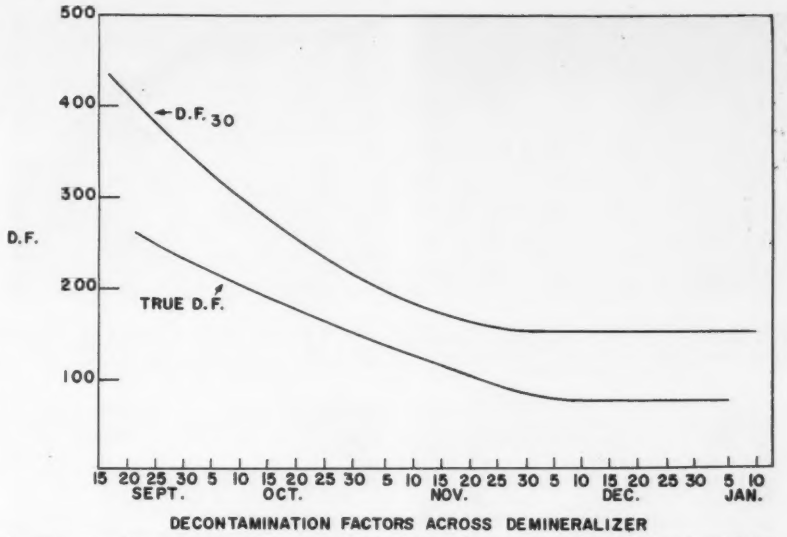


Figure 6—Comparison of average DF's measured 30 minutes after sampling and true DF's extrapolated to time of sampling.

quite hard to measure in low concentrations, decontamination factors have been determined for individual nuclides in an attempt to find an answer. Due to the time interval, these determinations have been primarily on longer-lived nuclides, such as $Co^{58}$ $Co^{60}$ $Cr^{51}$ and $Mn^{54}$ These have varied considerably, probably due to analytical error, but have furnished no basis for explanation.

It was thought at first, that the non-reproducible decay patterns on demineralizer effluent might be due to channeling or desorption of monovalent ions from the resin. A demineralizer that had been operated for about two months and subsequently taken off-stream due to a leaky weld was examined by taking pint samples from throughout the bed. The particulate crud was washed off the resin at The Oak Ridge National Laboratory and the resin and metallic activity measured. Preliminary data are shown in Table 1. Future analyses on other demineralizers in conjunction with in-plant tests at varying purification flow rates may help to explain the role of both the purification system and demineralizer in maintaining water purity, and the inter-relationship between system activity, corrosion and fouling, and crud deposition on system surfaces.

*Corrosion Products*

Chemical analysis for corrosion products circulating in the system indicated that minor amounts of iron, chromium, nickel, manganese, or cobalt were present. Analysis by colorimetric methods on samples concentrated 10-fold by evaporation showed only iron. As shown in Table 2, iron concentration varied from about .01 to .05 ppm, averaging 0.03 ppm over the first six months. Also shown in the same table are representative analysis on total dissolved solids. On samples concentrated by a factor of 20 to 40, total solids have been less than 2 ppm, averaging slightly under 1.0 ppm.

**Corrosion and Activity Test Program**

To reduce operational and maintenance problems, it is important that transport, activation, and deposition of corrosion products on primary system components be minimized. Operating experience with all pressurized water reactors has shown that long-lived radioactivity builds up on primary system surfaces with increased reactor operating time. Considerable effort is being devoted to the problem at several reactor installations, and as a result, a great deal of information has been obtained on the corrosion and activity problem. However, considerably more data will be required to completely understand all facets of the activity transport phenomena.

*Pipe Samples*

Specimens of piping removed from various locations in the primary system have been submitted to visual, metallographic, chemical, and radiochemical analysis. Visual examination has shown only a thin, tightly adherent, brownish

**TABLE 1—ORNL Analysis of APPR-1 Demineralizer Resin**

| Nuclide | RESIN ACTIVITY, dpm/gm | | | METALLIC ACTIVITY, dpm/gm | | |
|---|---|---|---|---|---|---|
| | Top | Middle | Bottom | Top | Middle | Bottom |
| $Mn^{54}$ | $2.8 \times 10^7$ | $5 \times 10^7$ | $7 \times 10^5$ | $1.7 \times 10^8$ | $1.2 \times 10^8$ | $4.4 \times 10^7$ |
| $Fe^{55}$ | $1.1 \times 10^7$ | $2.1 \times 10^7$ | $1.8 \times 10^7$ | $7.9 \times 10^8$ | $6.7 \times 10^8$ | $2.8 \times 10^8$ |
| $Co^{58}$ | $2.7 \times 10^6$ | $1.4 \times 10^7$ | $1.5 \times 10^6$ | $4.6 \times 10^8$ | $3.6 \times 10^8$ | $1.8 \times 10^8$ |
| $Co^{60}$ | $1.8 \times 10^6$ | $1.1 \times 10^7$ | $1.1 \times 10^6$ | $3.8 \times 10^8$ | $2.8 \times 10^8$ | $1.5 \times 10^8$ |

**TABLE 2—Corrosion Products* in APPR-1 Primary Coolant**

| Date | Total Dissolved Solids | Fe | Ni | Cr | Mn |
|---|---|---|---|---|---|
| 4/12 | .65 | .003 | 0 | 0 | 0 |
| 4/14 | .81 | .025 | . | ..... | .. |
| 4/16 | .85 | .05 | . | ..... | .. |
| 4/22 | .78 | ... | .. | ..... | .. |
| 4/30 | .91 | .05 | 0 | ..... | .. |
| 5/3 | .14 | .033 | 0 | ..... | 0 |
| 5/8 | .... | .02 | .. | ..... | .. |
| 6/2 | .56 | 0 | 0 | 0 | 0 |
| 6/3 | .57 | .04 | .. | ..... | .. |
| 6/4 | 1.97 | .032 | .. | ..... | .. |
| 6/5 | .54 | .057 | .. | ..... | .. |
| 6/7 | 1.4 | .... | .. | ..... | .. |
| 9/18 | .81 | .... | .. | ..... | .. |
| 9/19 | .... | .009 | .. | .002 | .. |
| 9/24 | .... | .004 | .. | .0006 | .. |
| 9/27 | .3 | .01 | .. | .001 | .. |
| 10/3 | .06 | .02 | .. | .004 | .. |

* In ppm.

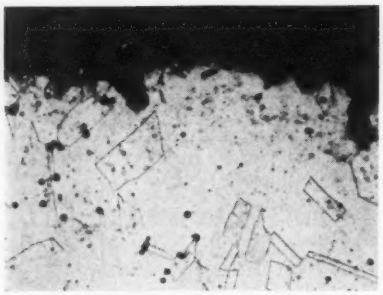

Figure 7—Photomicrograph of pipe sample removed from APPR-1 primary system. Original magnification, 500X; actual magnification after reduction for engraving purposes, 300X.

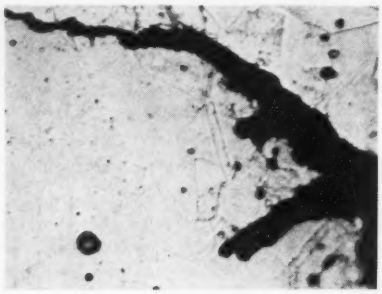

Figure 8—Photomicrograph of pipe sample removed from APPR-1 primary system. Original magnification, 1000X; actual magnification after reduction for engraving purposes, 600X.

Figure 9—Photomicrograph of pipe sample removed from APPR-1 primary system. Original magnification, 100X; actual magnification after reduction for engraving purposes, 60X.

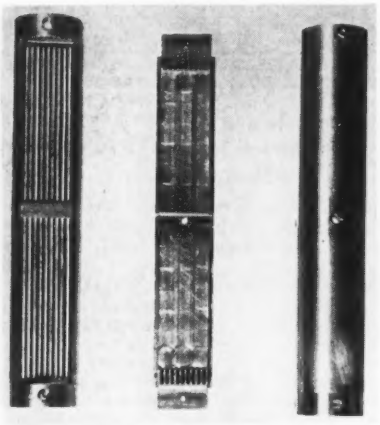

Figure 10—Specimen holder.

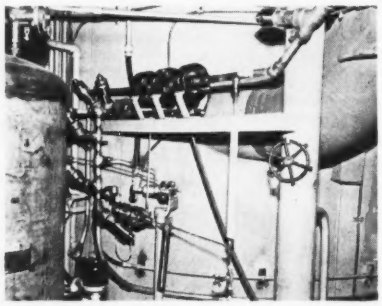

Figure 11—Test specimens and crud probe exposed to reactor inlet water.

**TABLE 3—Cutie Pie Readings at a Distance of Three Inches**

| | Upstream | Downstream |
|---|---|---|
| Over 304 specimens. . | 105 mr/hr<br>120 mrad/hr | 61 mr/hr<br>180 mrad/hr |
| Over 16-1 and carbon steel specimens. . . . | 240 mr/hr<br>475 mrad/hr | 64 mr/hr<br>190 mrad/hr |

film. A 30-inch piece of 1-inch, Schedule 80, Type 304 stainless steel pipe was removed from the purification system upstream of the blowdown cooler after eight months of reactor operation. Prior to removal, the section of pipe read 90 mr/hr, as measured by a cutie pie held in contact with the outer surface. Visual observation disclosed no evidence of pitting or loosely adherent material on the surface. The corrosion product film was brownish in color, with only a faint indication of any black oxide. The pipe was cut into various lengths for analysis, part being sectioned into 1-inch long specimens for reinsertion into the system. After two days time, these 1-inch sections had decayed so that the cutie pie gave readings of only 30 mr/hr and 39 mrad/hr at 3 inches on the closed and open window readings. Every two to four weeks, one of these pipe sections has been removed for examination.

Metallographic examination of the pipe samples has not disclosed much more than visual examination. Part of the pipe referred to above was polished, etched, and examined with a B & L Research Metallograph at magnifications up to 1000 diameters. As shown in Figure 7, only a very thin oxide scale was evident when the specimen was etched in oxalic acid and examined at 500 diameters. To determine if foreign material was deposited in the surface seams of the pipe, the section was examined at 1000 diameters. Figure 8 shows the photomicrograph at this magnification; the seams were filled with oxide scale but there was no evidence of crud deposition in the seams.

Previously, the many small seams produced in the seamless pipe during fabrication had been suspected of trapping crud and contributing to the activity levels mentioned previously. As illustrated by Figure 9, a photomicrograph of the same pipe at 100 diameters, seams are readily available. For comparison purposes, unused sections of the same pipe were similarly examined, but no appreciable differences were evident. The seams were filled with scale to the same extent as those in the in-plant specimens. A small amount of surface scale had been removed from the in-plant specimens by the erosive action of the water, but, otherwise, control and test specimens have been essentially similar. These and similar results on crud filters and specimens lend credulence to the fact that an atom exchange phenomena is occuring throughout the system. However, more data are needed to confirm this.

*Steam Generator*

To study corrosion-erosion and deposition, a section of the Type 304 stainless steel baffle plate in the steam generator water box was removed for examination after seven weeks of reactor operation. As measured with a cutie pie, the baffle plate read 280 mr/hr. Examination disclosed results similar to the pipe samples discussed previously—the brownish corrosion product film was tightly adherent, with no evidence of erosion or deposition.

*Metal Test Specimens*

To determine corrosion and deposition rates on various materials of construction, metal coupons were inserted in the primary system. The original specimen holders are similar to those fabricated for the high temperature, high pressure corrosion test loops at Alco and most other organizations. As shown in Figure 10, the holders consisted of eight separate pieces, excluding the screws. While this design was satisfactory for non-radioactive work, it proved very unhandy when both the holders and specimens were contaminated and had to be handled with rubber gloves. Several improved designs have been made, and additional redesigning is continuing to develop a cheap, easy-to-use holder that has the desired flow and velocity patterns with minimum possibility of erosion or galvanic couple problem.

The specimen holders have been inserted at various locations in the primary system. Figure 11 illustrates a typical set-up in the vapor container. Shown to the far right is a section of the reactor inlet piping. The specimen holders are inside the flanged holders. A by-pass 45 square-inch cylindrical crud probe, turbine-type flowmeter and associated solenoid valves also are visible.

To date, only four materials have been tested. Type 304 stainless steel, Croloy 16-1, low manganese A-212-B, and a general carbon steel. Every two to four weeks, depending on reactor operation, a specimen of each type has been removed and replaced with a new coupon. As yet, insufficient time has elapsed to permit any quantitative comparison of corrosion and deposition rates. On the original samples, however, it has been possible to formulate some tentative observations and conclusions.

Visual observations alone have disclosed several interesting points. Figures 12 and 13 illustrate results typical of observations found for most specimens. These samples were removed after exposure for about 1200 hours to primary coolant upstream and downstream of the purification cooler. Temperatures of the water were 432F and 105F respectively. As far as has been determinable, this water is similar in composition to that circulating through the main primary system. Removal time for the specimens exposed to 432 F water was approximately 32 hours after shutdown; the downstream samples were removed 35 hours after shutdown. For these particular specimens, upstream of the cooler the water flowed past the 16-1 and car-

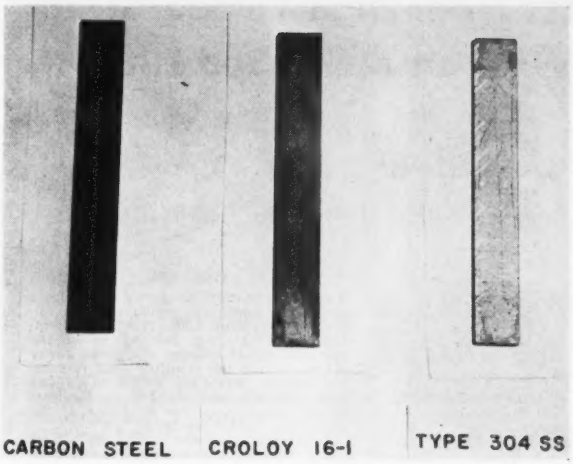


Figure 12—Specimens exposed to 432 F primary coolant for 1200 hours.

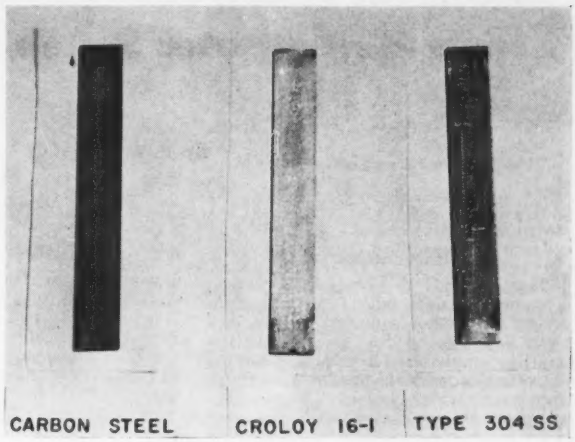


Figure 13—Specimens exposed to 120 F primary coolant for 1200 hours.

bon steel specimens before passing over the 304 coupons; downstream of the cooler this pattern was reversed.

When the holders were opened, cutie pie readings at 3 inches are shown in Table 3.

Stainless steel specimens had a light brown tightly adherent oxide film; however, contrary to expectations, the color of the film on specimens exposed to the higher temperature generally has not been as dark as on those exposed at lower temperatures. Crud deposition on upstream samples always has completely blackened the 16-1 and carbon steel specimens and has been very much in evidence on the 304 coupons. On downstream samples, crud deposition has been heavier on the 16-1 and carbon steel than on the 304, but the metal is visible. As may be seen by examining the carbon steel specimen in Figure 13, the flow pattern is quite visibly outlined by the deposited crud. These photographs were made after the specimens had been wrapped and shipped from Ft. Belvoir to Schenectady and, unfortunately, the crud deposition patterns had been rubbed off by the filter paper in which each specimen is wrapped. When the specimens are first removed, the deposited crud clearly outlines the flow patterns—even on the upstream coupons that are entirely covered.

Of the specimens removed to date, there has been no evidence of galvanic effect where the 16-1 or carbon steels contact the Type 304 stainless holder nor has any evidence of pitting or erosion been apparent. Weight gains and descaled weight losses are determined for each specimen removed; results to date have not disclosed any unexpected results.

*Conclusion*

Operation of the APPR-1 over the past year has provided considerable information on the relationship between circulating corrosion product activity, system activity, and purity of the reactor coolant. Except for a small in-leakage of air into the make-up water, the purification system has exceeded design intent. Continuously removing about 0.07 percent of the total primary flow, passing it through a mixed bed demineralizer and reintroducing it as makeup has been sufficient to minimize corrosion and its associated problems of deposition on heat transfer surfaces and system activity.

From all indications, it appears that the corrosion rate of system components has been less than the originally estimated 5 mg/dm²/mo. The mixed bed demineralizers have been effective not only as ion exchangers and crud filters, but also have demonstrated their ability to remove activity from the water. Although extensive investigations are in progress to determine the effect of purification system operation on corrosion and circulating crud activities, results to date are inconclusive. From the proposed studies, attemps will be made to relate water purity requirements—during both normal operation and local boiling conditions—with deposition on heat transfer surfaces, specific activity of the crud, and general crud levels throughout the system. There are indications, however, that the purification system does not have an opportunity to remove all circulating crud but competes with primary system surfaces.

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# Removal of Corrosion Products From High Temperature, High Purity Water Systems With an Axial Bed Filter

By R. E. LARSON* and S. L. WILLIAMS*


## Abstract

The concentration of corrosion products and other impurities which produce undesirable radionuclides must be maintained at extremely low values in the primary coolant systems of nuclear power plants to keep the resulting dose rate below certain maximum values. This has been normally accomplished in the past by low temperature ion exchange of the pressurized water coolant.

Development of an axial bed filter which can remove radioactive corrosion products from high purity pressurized water coolant at operating temperatures is described. 8.4.5


## Introduction

THE OPERATING experience gained to date with both full scale pressurized water nuclear plants and in-pile loops used for fuel irradiation tests has emphasized the importance of controlling corrosion products in high temperature water coolant. The purification problem associated with the corrosion product removal is two-fold. The concentration of corrosion products in the coolant must be held to levels which will not result in excessive deposition on fuel surfaces or close moving components, and the radioactive corrosion product nuclides with long half-lives must be removed to prevent the buildup of excessive long-lived radioactivity.

The experience and measurements obtained from in-pile loop fuel irradiation tests and plant operation has shown that maintenance of corrosion product concentrations below one or two parts per million will result in trouble-free operation of close moving components such as control drive mechanisms and negligible increase in fuel temperature due to corrosion product deposits. The problem of minimizing the buildup of long-lived radioactivity through coolant purification is not fully understood. The buildup of long-lived radioactivity results from the deposition of corrosion product nuclides such as Cobalt[60] with a 5.3 year half-life on the inner surfaces of the coolant piping and in stagnant piping configurations. This radioactivity is not important during plant operation, but makes maintenance and repair work difficult after the plant has been shutdown. Concentrating as much of the long-lived nuclides as possible in a shielded purification unit may act to reduce the accumulation of long-lived activity in the remainder of the system.

Present operating pressurized water plants all utilize mixed anion and cation exchange resin for affecting coolant purification. The ion exchange resin has shown good efficiencies for removing the corrosion products in the coolant passing through the bed. The use of ion exchange resin for coolant purification in large systems has two disadvantages. The first disadvantage is the poor thermal resistance of the mixed resin, making it necessary to cool the influent to the ion exchange resin to 120-130 F. Since most pressurized water plants operate at temperatures around 500 F, sizeable heat exchange equipment can be required depending upon the purification flow rate. Temperature monitoring and protective devices are required to prevent accidental overheating of the resin.

The second disadvantage of ion exchange purification is the relatively high cost associated with the resin. Since the resin becomes severely contaminated with long-lived radioactivity, regeneration has not been considered practical and new resin must be added every few months.

This paper describes the application and testing of an axial bed filter containing low cost magnetic iron oxide for effecting the normal coolant purification in large pressurized water plants at operating temperatures. Concurrent testing of similar units also has been carried out by the Westinghouse Atomic Power Department.[1]

The selection of magnetite as a purification media for high temperature, high pressure water systems was based on tests of natural magnetite, alumina, zirconia, graphite, rutile ($TiO_2$) and a mixture of iron oxide and alumina by Westinghouse Atomic Products Department and Knolls Atomic Power Laboratory. Magnetite appeared to be the most stable material, demonstrating a lesser degree of leaching and exhibiting an ability to maintain acceptable low crud levels. Simultaneously with the bed filter work, an investigation of magnesia or magnesium metal as an agent for holding the pH of the coolant at a desired value above 8.0 was carried out.

## Test Apparatus

*Recirculating Loop Description*

**Out-of-Pile.** Four of the six tests connected with the bed filter were carried out in test facility TF-20, a recirculating water loop, operating at 2200 psi pressure and about 550 F temperature. The

* General Electric Company, Knolls Atomic Power Laboratory, Schenectady, N. Y.

**TABLE 1—Comparison of TF-20 and KAPL-30 Bed Filter Tests**

| RUN | | Loop | Time hrs | COOLANT Temp. | COOLANT Flow, gpm | BED FILTER Flow gpm | BED FILTER Loading gpm/sq ft | BED FILTER Total Gallons | BED FILTER Composition By Weight | BED FILTER Gms | Insoluble Level* ppm | $\Delta p$ Inches |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Out of Pile | HB-2 | TF-20 | 1015 | 500 F | 17 | 0.1 | 8.1 | 6350 | 10 $Fe_3O_4$<br>1 MgO | 2200<br>500 | 0.5 | .... |
| | HB-3 | TF-20 | 620 | 500 F | 17 | 0.1 | 8.1 | 3732 | 10 $Fe_3O_4$<br>1 Mg | 1833<br>182 | 1.1 | 21 |
| | HB-4 | TF-20 | 385 | 500 F | 17 | 0.1 | 8.1 | 2300 | 10 $Fe_3O_4$<br>1 Mg | .... | 0.3 | 21 |
| | HB-5 | TF-20 | 265 | 500 F | 17 | 0.1 | 8.1 | 1580 | 10 $TiO_2$<br>1 Mg | .... | 4.0 | 55 |
| In Pile | Run 1 | KAPL-30 | 780 | 400 F to 560 F | 105 | 0.2 to 0.3 | 9.2 to 13.8 | 11,688 | 10 $Fe_3O_4$<br>1 MgO | .... | 1.5-4.1 | psi<br>> 20 |
| | Run 2 | KAPL-30 | 330 | 530 F | 105 | 0.25 | 46 | 4980 | 20 $Fe_3O_4$<br>1 Mg | .... | 2.2 | 35 |

**NOTES:** * Insoluble corrosion product level in loop water.

TF-20 Bed Filter 1.5 inch diameter, 30 inch deep, volume = .0307 cu ft.
Material of construction — A-106, carbon steel.
Loop Volume — 3.55 cubic feet.
Main Loop Piping — 1" Schedule 80.
TF-20 Makeup Water — Demineralized, Deoxygenated.

KAPL-30 Bed Filter — Run 4:2 inch diameter, 30" deep, Volume = 0.0545 cu.ft.: Run 5: 1 inch diameter, 30" deep Volume = .0136 cu.ft.
Material of Construction — Carbon steel.
Loop Volume — 9.36 cubic feet.
Main Loop Piping — 2½" Schedule 160.
Makeup Water — Demineralized, Deoxygenated.

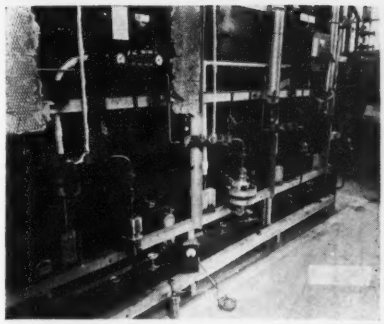

Figure 1—TF-20 hot bed filter columns.

facility was constructed of A 106 Grade B carbon steel and consists of a heater, pressurizer, and a purification circuit. Immersion heaters were used to maintain the loop temperature and a steam pressurizer at the desired pressure. The flow through the main loop was about 17 gallons per minute. Table 1 compares the operating parameters for the in-pile and out-of-pile tests.

The columns in which the tests were carried out are shown in Figures 1 and 2. The ten-to-one weight ratio of magnetite to magnesium or magnesia and rutile ($TiO_2$) to magnesium was contained in the internal sleeves (with Neva Clog filter support plate) shown in Figure 2 to simplify charging and removal and to reduce the loss of collected crud. The flow through the filter was 0.1 gallon per minute. The ion exchanger was used to purify the loop water during the leaching periods prior to tests.

Insoluble corrosion product and water samples were obtained using a graphite precoated crud filter shown in Figure 3 and a nickel plated vessel, respectively. Details are described in Reference 2.

**In-Pile.** The in-pile facility is also a recirculating high temperature, high pressure test loop constructed of carbon steel. It is located at the Materials Testing Reactor in Idaho. A schematic flowsheet is given in Figure 4. Corrosion and fuel test assemblies can be separately charged to and discharged from the 3 parallel in-pile channels in the reentrant thimble. The flow through the main loop was 105 gallons per minute. The by-pass purification system contains a hot bed filter, and an ion exchange column. Composite insoluble corrosion product and water samples downstream of the in-pile tube and of the bed filter were collected using the previously mentioned nickel sintered-metal, graphite precoated filter and nickel-plated vessel.

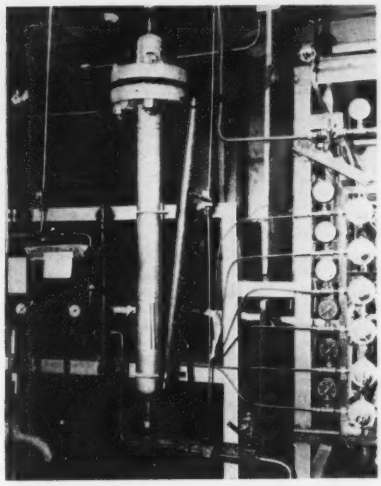

Figure 2—TF-20 sleeve and filter body.

The Materials Testing Reactor operates in cycles of three week duration. During the shutdown time at the start of each cycle the loop water normally remains circulating (except for maintenance or changing of test assemblies) and a temperature of 300 F is maintained with electrical heaters.

*Procedure*

**Out-of-Pile.** The magnetite was obtained from the C. K. Williams and Company of Easton, Pa. and had the following properties:

Vendor's Sample Code: TS-1712-4
Total Iron as Fe: 71.5 percent
Magnetite ($Fe_3O_4$): 97.5 percent
Bulk Density: 161 lbs per cu ft
Screen Analysis:
6.1 percent on 40 mesh
42.7 percent on 50 mesh
25.0 percent on 60 mesh
11.8 percent on 70 mesh
14.3 percent through 70 mesh

Normally this magnetite was washed with demineralized water and poured into a water-filled sleeve of 1.5 inch diameter to a depth of 37 inches. After installing the column the loop was operated with a 0.1 gallon per minute purification flow rate passing through the conventional low-temperature mixed bed, ion exchange resin (Rohm and Haas Company XE-169 and XE-78, 40-70 mesh) until a constant value of water specific resistivity was obtained.

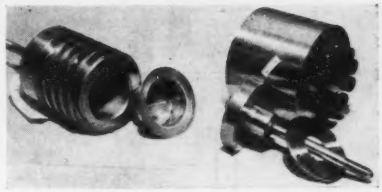

Figure 3—Hot corrosion product filter.

In addition at the start of runs HB-4 and HB-5 bed leaching operations also were performed. Following the leaching the loop was drained and filled with fresh make-up water. When the loop had attained normal operating temperatures, flow was started through the bed filter at a rate of 0.1 gpm. Samples of water were taken upstream and downstream of the bed filter for measurement of pH, resistivity and chemical composition. The water entering and leaving the column was periodically sampled for insoluble corrosion product and dissolved solids by use of the corrosion product filter. Analysis of water samples was normally done by spectrographic procedures.

**In-Pile.** The magnetite previously leached in the out-of-pile loop was washed with demineralized water and poured into a water-filled sleeve of 1 or 2 inch diameter to a depth of 30 inches. The Run 1 and Run 2 studies were made on beds having 10 to 1 parts by weight of magnetite to magnesia and 20 to 1 parts of magnetite to magnesium metal, respectively. Because of the suspected leakage of filter media into the coolant a 200 mesh stainless steel screen was added to the Neva Clog support plate before the Run 2 test. For normal startup, flow was begun through the bed filter at a rate of 0.2 to 0.3 gpm while the loop temperature was being raised to operating conditions. Samples of water were taken from taps upstream and downstream of the bed filter. The insoluble corrosion product samples were one hour per day, three day composites from the main coolant line and downstream of the hot bed filter. A gross count is performed at the MTR Site on 1 ml portions of all water samples. Radiochemical and chemical spectrographic analyses on insoluble corrosion product and water samples were performed at KAPL. These results are summarized in Tables 2, 3 and 4. Flow and pressure drop relations, loop pH and resistivity, effect on flow through the fuel elements, corrosion product levels, the activity decontamination factor across the filter and bed life were investigated.

**TABLE 2—Hot ICP* Filter Samples**
**(KAPL—30 Runs 1 and 2)**

| HCF NO. | Date | Collection Time, Min. | Water Temperture, Degrees F | Radiation Level of Basket, mr/hr | Flow Rate, gpm | ICP* LEVELS | | Ion Exchange |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Weight, mg | ppm | |
| 304- 1 | 5/21,22 | 86,85 | 244 | 30 (3/16) (3") | .083 | .... | .... | IX |
| 304- 2 | 7/1,3 | 172,85 | 350,458 | 400 (4") | .083, .096 | 318 | 4.15 | BF |
| 304- 3 | 7/25,26 | 86,90 | 445,453 | 500 (4") | ..... | 77 | 1.47 | BF |
| 304- 4 | 7/29,31,8/2 | 85,85,90 | 458,250,240 | 5000 (4") | .096, .083 | 94 | 1.2 | IX |
| 304- 5 | 8/12,14,16 | 85,85,88 | 465,450,445 | 3000 (4") | .096 | 70.5 | 0.91 | IX |
| 304- 6 | 8/20,21,23 | 85,60,60 | 440,449,458 | 3000 (6") | ..... | 44.8 | 0.66 | IX |
| 304- 7 | 9/4,6 | 85,30 | 450,363 | ..... | ..... | Basket | Empty | IX |
| 304- 8 | 9/9,11,13 | 60,60,60 | 453,460,460 | 250 (4") | .066 | 16.7 | 0.56 | IX |
| 305- 9 | 9/23,25,27 | 60,60,60 | 325,345,267 | 700 (4") | .09 | 37.1 | 0.6 | IX |
| 305-10 | 9/30,10/2,4 | 60,60,60 | 260,273,273 | 1000 (4") | .09 | 19.4 | 0.33 | IX |
| 305-11 | 10/14,16,18 | 60,60,60 | 480,428 | >5000 (4") | ..... | 121 | 2.14 | BF |
| 305-12 | 10/21,23 | 84,65 | 430,430 | ..... | .095 | 114 | 2.34 | BF |

* Insoluble Corrosion Products in Loop Water.

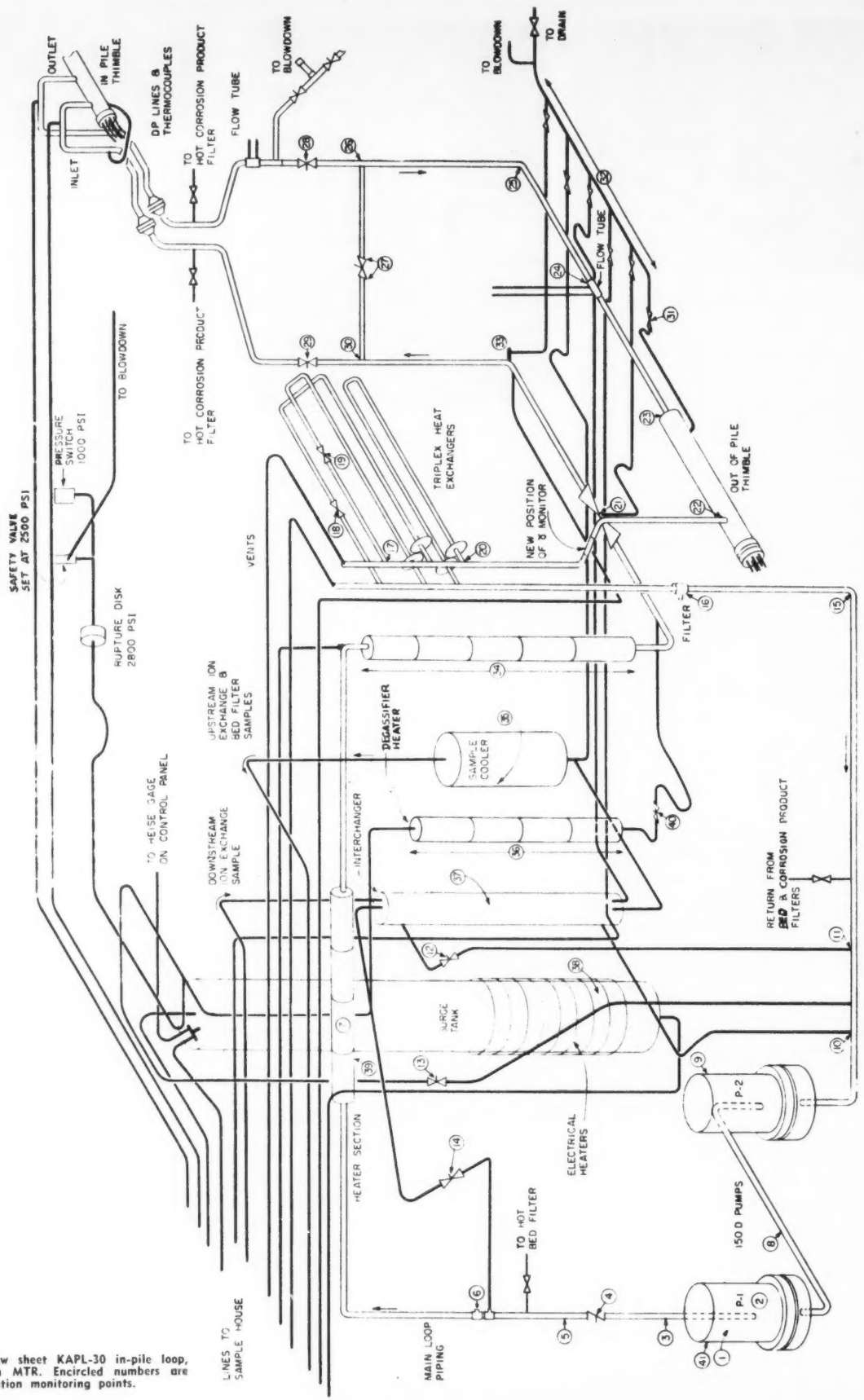


Figure 4—Flow sheet KAPL-30 in-pile loop, HB-1 position MTR. Encircled numbers are radiation monitoring points.

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**TABLE 3—Hot ICP* Filter Samples Downstream of Axial Bed Filter (KAPL—30, Runs 1 and 2)**

| HCBF No. | Date | Collection Time, Minutes | Water Temp, Degrees F | Radiation Level, mr/hr | Flow Rate, gpm | ICP* LEVELS | | Bed Filter Weight Ratio |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Weight mg | ppm | |
| 304-1..... | 7/15 | 129 | 170 | 400 (4") | .062 | Basket | Empty | 10$Fe_3O_4$ to 1 MgO |
| 304-2..... | 7/22 | 110 | 515 | 15 (7/26) | .... | 149 | 3.4 | Same |
| 304-3..... | 7/29 | 28 | 520 | 90 (4"8/2) | .066 | 53.8 | 9.6 | Same |
| 305-4..... | 10/14,18 | 30 | 470,485 | 120 (4") | .07 | Basket | Empty | 20 $Fe_3O_4$ to 1 Mg |
| 305-5..... | 10/23 | 60 | 480 | ..... | .08 | 15.7 | 0.86 | Same |

* Insoluble Corrosion Product.

**TABLE 4—A Study of Fission Product and Corrosion Product Decontamination Across the Axial Bed Filter Liquid Samples***

| ISOTOPES | SAMPLE CODE DATE AND TIME | | | | Decontamination Factor = Activity UHBF / Activity DHBF | |
|---|---|---|---|---|---|---|
| | UHBF** 305-8A 10/23 at 1609, d/m/ml x $10^{-6}$ | | DHBF** 305-8 10/23 at 1552, d/mml x $10^{-6}$ | | | |
| | Sample I | Sample II | Sample A | Sample B | Maximum | Minimum |
| **(A) FISSION PRODUCT** | | | | | | |
| $I^{133}$..... | 3.24 | 3.59 | 2.34 | 1.98 | 1.8 | 1.4 |
| $I^{131}$..... | 1.50 | 1.45 | .807 | .707 | 2.1 | 1.8 |
| $Sr^{91}$..... | .341 | .326 | .328 | .341 | 1.04 | 0.96 |
| $Sr^{89}$..... | .037 | .039 | .035 | .0356 | 1.1 | 1.04 |
| $Ba^{139}$..... | .720 | .787 | .777 | .780 | 1.01 | 0.92 |
| $Cs^{139}$..... | .920 | 1.10 | 1.80 | 4.20 | 0.61 | 0.22 |

| (B) CORROSION PRODUCT | Decontamination Factor | |
|---|---|---|
| | Maximum | Minimum |
| $Sb^{124}$..... | 10,000 | ..... |
| $Hg^{203}$ (source of Hg unknown)..... | 1,000 | 30 |
| $Fe^{59}$..... | 113 | 5 |
| $Co^{60}$..... | 34 | 2.4 |
| $Zr^{95}$-$Nb^{95}$..... | 15 | 1.7 |

* KAPL-30, Run 2.

** NOTE: **UHBF** is upstream bed filter water sample; **DHBF** is downstream bed filter water sample.

A solubility-temperature curve for magnesium oxide (from Reference 4, work of M. L. Jones) is shown in Figure 5. The work by Seidell mentioned in this figure is cited in Reference 5.

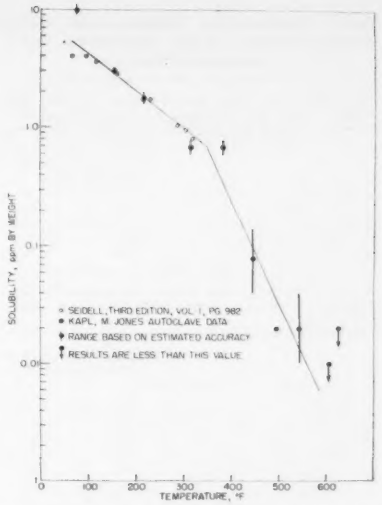
SOLUBILITY, ppm BY WEIGHT
TEMPERATURE, °F
SEIDELL, THIRD EDITION, VOL. 1, PG. 982
KAPL, M. JONES AUTOCLAVE DATA
RANGE BASED ON ESTIMATED ACCURACY
RESULTS ARE LESS THAN THIS VALUE

**Figure 5—Solubility temperature curve for magnesium oxide reported as ppm of Mg.**

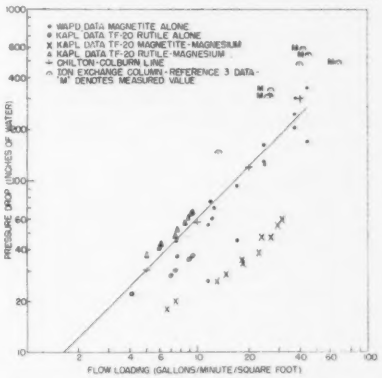
WAPD DATA MAGNETITE ALONE
KAPL DATA TF-20 RUTILE ALONE
KAPL DATA TF-20 MAGNETITE-MAGNESIUM
KAPL DATA TF-20 RUTILE-MAGNESIUM
CHILTON-COLBURN LINE
ION EXCHANGE COLUMN-REFERENCE 3 DATA-
"M" DENOTES MEASURED VALUE
PRESSURE DROP (INCHES OF WATER)
FLOW LOADING (GALLONS/MINUTE/SQUARE FOOT)

**Figure 6—Pressure drop versus flow loading for WAPD and KAPL hot bed filter tests.**

## Discussion

*Pressure Drop*

Flow loading-pressure drop data for WAPD and KAPL tests on magnetite filter beds are plotted in Figure 6. For viscous flow, the theoretical slope (Chilton-Colburn correlation) of the curves would be 1.0 so that fair agreement with the theoretical has been obtained. WAPD data for 30 inch magnetite beds, same bed depth and particle size (40 to 70 mesh), give pressure drops larger by a factor of two than those encountered in the TF-20 tests. The increased pressure drop of the rutile bed over that of the magnetite bed is attributed to the smaller particle size (less than 120 mesh) of the former. The rutile-magnesium filter had a 50 percent higher pressure drop than did the rutile alone.

Flow loading pressure drop data for ion exchange beds were obtained from Reference 3 and also are plotted in Figure 6. For similar flow loadings and column heights the pressure drop through the 30 mesh ion exchange is about a factor of 2 greater than through the bed filter. It is to be noted that Reference 3 data on ion exchange flow loadings are considerably higher than the 3 to 12 gpm/sq ft conventionally recommended by the resin manufacturers.

*Insoluble Corrosion Product Levels and Flow Loadings*

Initial magnetite studies at high pH (maintained by injections of ammonium hydroxide) in the out-of-pile loop showed bed filter effluent, insoluble corrosion product levels consistently below 0.15 ppm. This demonstrates the good filtering efficiency of the bed filter.

The insoluble corrosion product level of the in-pile loop water was 1.2 to 4.1 ppm for hot bed filter purification, and 0.3 to 0.9 ppm for ion exchange purification with mixed bed ammonium form resin. The difference is attributed to the escape of both particulate magnetite and magnesium hydroxide through the bed filter support plate. The presence of these materials instream has been shown in the spectrographic analysis of the graphite-micrometallic filter samples. A magnesium material balance on the column also showed that 35 of initial 58 grams were lost to the coolant. This is far more than could be accounted for by solubility alone.

Flow loadings for the bed filter are given in Table 1. The 46 gpm/sq ft loading used in the Run 2 test is in the optimum range for high filtration efficiency of the insoluble corrosion products. The flow loadings for the ion exchanger were 2.8 to 14.2 gpm/sq ft.

The rutile test (HB-5) in the out-of-pile loop maintained an insoluble corrosion product and rutile level in the loop water of 4.0 ppm. Analysis showed that 90 percent of the insoluble corrosion product was titanium dioxide. Leakage of the $TiO_2$ through the Neva-Clog retention screen proved to be the cause of this level.

Correcting for the leakage of filter media through the bed support it is apparent that the insoluble corrosion product levels for hot bed filter and for ion exchange purification are of equal magnitude.

*Effects of pH on Purification and pH Control With the Bed Filter*

**Data From the Out-of-Pile Loop Test.** The effects of pH on purification with the bed filter are shown in Table 5. Low pH had little effect on decreasing the efficiency with which the bed filter removed filterable corrosion products. Measurement of the concentration of non-filterable iron and manganese in the column influent and effluent, showed that the concentration of these elements increased with a pH lower than 7, in both influent and effluent. Since the solubility of these elements increases in an acid environment, this increase is expected. If this increase in solubility is taken into account, the over-all purification efficiency of the bed filter actually increases with the increasing pH until the corrosion product solubility becomes constant.

Table 5 shows the insoluble corrosion product levels and the manganese and iron concentrations in the filtrate for the out-of-pile tests on a magnetite bed filter. Part A illustrates that for conditions of pH greater and less than 7 (range 6 to 9.5) the filter has good efficiency for insoluble removal attaining filterable corrosion product levels of less

**TABLE 5—Corrosion Product and Water Sample Results (KAPL Out-of-Pile Tests. Magnetite Filter.)**

**(A) Insoluble Corrosion Product Levels Upstream And Downstream of Magnetite Filter**

| | Average Insoluble Corrosion Product Levels, ppm | |
|---|---|---|
| pH→ | >7 | <7 |
| Upstream Sample | 2.23 | 2.50 |
| Downstream Sample | .065 | .015 |

**(B) Filtrate Samples From Corrosion Product Filters Upstream And Downstream of Magnetite Filter**

| | Average Soluble Fe and Mn Levels, ppm | |
|---|---|---|
| pH→ | >7 | <7 |
| Mn, Upstream | .022 | .035 |
| Mn, Downstream | .010 | .020 |
| Fe, Upstream | .486 | .462 |
| Fe, Downstream | .143 | .257 |

than 0.1 ppm in the filter effluent. Direct measure of filtration efficiency is difficult to make because of the effect sampling time has on filterable corrosion product concentrations in spite of line flushing prior to sampling. Samples taken over a short period of time (15 to 30 minutes) yielded much higher concentrations than those taken over several hours.

Examination of Part B of Table 5, the filtrate samples up and downstream of the magnetite filter, shows that the magnetite material demonstrates no ability to remove appreciable amounts of soluble impurities. The removal ability evident is probably due to filtration of the precipitated materials rather than by ion exchange or adsorption. The concentrations of Fe and Mn in the samples downstream of the magnetite filter approach the expected solubilities as a limit. It was found that the solubility of iron and manganese is quite sensitive to pH and that a pH greater than 7 is needed to reduce the non-filterable manganese concentration to .01 ppm downstream of the bed filter.

**Most Pressurized Water Plants.** The coolant in most pressurized water plants will be on the basic side due to the presence of small amounts of ammonia which are synthesized from residual nitrogen from air contaminated makeup and the hydrogen produced by the metal-water corrosion reaction. The data show that under these conditions the concentration of soluble iron and manganese corrosion products in the column effluent will be in the order of 0.1 ppm and 0.005 ppm, respectively. The particulate corrosion products in the effluent ran less than 0.1 ppm on the average.

Since experience has indicated that the corrosion product release rate can be further reduced by elevating the coolant pH above 9.0, an attempt was made to incorporate magnesium oxide or magnesium metal with the magnetite as an additive to increase the pH of the coolant. It was hoped that the magnesium oxide would slowly dissolve into the coolant, maintaining the requisite pH. As indicated previously, both out-of-pile and in-pile tests were run with this mixture. The tests showed that insufficient magnesium oxide would dissolve in the water above 450 F to hold the pH above the desired value of 9.0. Also, the preferential deposition of the magnesium compounds on heated surfaces stemming from the inverse temperature solubility of magnesium hydroxide created an additional problem rather than simplifying the system.

*Comparison of Ion Exchange and Hot Bed Filter Purification*

Examination of the filtrate samples from the basket filter for both the Run 1 and Run 2 bed filter tests in KAPL-30 did not show any significant trend as to differences in long-lived gross activity between filter and ion exchange performance.

Samples of ion exchange resin and hot bed filter media removed from the KAPL-30 tests have been dried and subsequently counted for gross count. Comparing these counts on a volume basis to correct for the large density difference between resin and filter media shows the results to be as follows:

IX Resin: $1.5 \times 10^6$ c/min/ml of resin
HBF Media:
$2.0 \times 10^6$ c/min/ml of filter media

The bed filter is at least the equal of the ion exchange column when comparing the pickup of long-lived corrosion product activity from the water.

During the Run 2 test, decontamination factors across the hot bed filter for fission products and for corrosion products were determined. These are reported in Table 4. No decontamination factor was found for the fission products $Cs^{139}$, $Ba^{139}$, $Sr^{89}$ and $Sr^{91}$.

The following comparison of the cost of magnetite and ion exchange resin points out a significant advantage in the former based on replacement without backwashing or regeneration.

| Material | Cost/cu ft | Bulk Density lbs/cu ft |
|---|---|---|
| Magnetite | $6/cu ft | 160 |
| Ammonium Form Mixed Bed Ion Exchange Resin | $130/cu ft | 45 |

## Summary

While the use of ion exchange resin has been shown to be satisfactory for removing corrosion products and their radioactive nuclides from the coolant of water cooled nuclear power plants, the high unit cost of the resin and the need for large heat exchange units due to its thermal instability, make high temperature purification with a low cost media attractive for large purification flows. The testing of an axial bed filter charged with low cost magnetic iron oxide has shown that this material not only possesses the desired thermal stability, but is highly effective in removing corrosion products and their radioactive nuclides under conditions found in pressurized water plants. On a volume basis (ml resin to ml magnetite) a test showed that the bed filter removed as much long-lived activity from a coolant stream as did an ion exchange resin. Satisfactory decontamination factors for the following long-lived corrosion product nuclides were found: $Fe^{59}$, $Co^{60}$, $Zr^{95}$-$Nb^{95}$ and $Sb^{124}$. The filter bed was not effective in removing soluble fission products or other soluble impurities. The use of a small flow ion exchange unit in conjunction with the large flow filter would be required in those applications where soluble fission product removal was needed.

Additional tests on this unit conducted at this Laboratory and by the Bettis Laboratory of the Westinghouse Atomic Power Department have shown that the pressure drop through the filter bed is comparable to that experienced with ion exchange resin, and that this type of unit is effective in maintaining the concentration of corrosion products circulating in the coolant below 1 ppm. The data show that the filtration efficiency of the bed is not affected by pH. Attempts to use magnesium with the magnetite to maintain elevated coolant pH as well as to effect purification were unsuccessful.

## Acknowledgments

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Particular thanks are due to D. Dutina, and W. C. Judd for their efforts in obtaining the radiochemical results, and to A. A. Sugalski for his contributions in the early stages of this investigation. The significant work of M. L. Jones on temperature-solubility of magnesium oxide is graciously acknowledged.

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# Some Relations Between Deposition And Corrosion Contamination In Low Make-Up Systems for Steam Power Plants*

By E. S. JOHNSON* and H. KEHMNA**

**Abstract**

A mechanism is postulated which indicates that the ratios and interactions of contaminants in low make-up systems of steam power plants are more significant with respect to deposition than the absolute amount of contaminants present. Three examples are cited in support of this theory. It is shown that mechanisms based upon the thermodynamics of the soluble ions from the corrosion of materials of construction can qualitatively account for both the form and composition of the deposits from high purity water in large steam generating stations. In so far as trouble from deposits is concerned, the ratio of copper to iron seems more important than the absolute concentrations of either. Small variations in the concentration of other ions do not seem to be of any great importance. 3.4.3

## Introduction

PROBLEMS RELATING to corrosion and deposition in feedwater and boiler circuits of large power plants have become more and more acute as initial steam pressures have continued to increase.

This discussion explores the transportation and deposition of corrosion products in the high purity water of large, low-make-up steam generating stations. The term "high purity" as used here will be taken to mean total mineral contents of the order $10^{-7}$ to $10^{-5}$ gram mols per kilogram of water. The materials considered will be limited to the major constituents of the materials of construction (i.e., iron, copper, zinc and nickel.)

The whole phenomenon of initial corrosion will be dismissed with the simple statement that the bivalent ions are formed from the metal by water acting as an acid in the Broensted sense. It will be admitted at the outset that dissolved gases, differential concentrations and the other tools of corrosion affect the general and local rates. After this the matter will be dropped. This attitude is taken because:

1. Initial corrosion is somewhat like a fly buzzing around the ears, while transport and unpredictable deposition represent the man with the club waiting to deliver the knockout blow.
2. It can be shown that, due to the extremely low solubilities of the reaction products of the initial corrosion products, minimizing initial corrosion does not necessarily minimize deposition.

The final corrosion phenomenon, that is the reaction in and under the deposits which result in ultimate failure under heat transfer, also will be ignored in this discussion, because:

1. This is no longer the chemistry of high purity water and hence lies outside the area of consideration.
2. The battle is already lost when this point is reached, although the reactions are well understood.

In the absence of *gross* contamination in the form of calcium, magnesium, silica, oxygen, etc., the authors' principal thesis is: Deposition permitting many years of successful operation, contrasted with deposition that leads to failure under heat transfer in a relatively short time, depends essentially upon the ratio of copper to iron in the water and not upon the absolute levels of either.

When deposits are examined, three overlapping classes are found:

A. Dense, brittle, tenaciously adherent deposits
B. Porous, friable, loosely adherent deposits
C. Non-adherent powders or sludges which may, on a micro scale, be either dense (C-1) or porous (C-2).

Since all three classes contain essentially the same elements, this suggests that at least two formation mechanisms are in operation.

It would appear that any really serviceable mechanism to account for the formation of a dense, brittle, tenacious deposit must operate by crystal formation from a soluble ionic state. It is proposed to account for the loosely adherent deposits by dehydration in place, of precipitates first formed by ionic reactions from solution. It also is proposed to account for the non-adherent sludge as a mixture of intra-solution precipitates arising from both ionic reactions and dehydration. It will be recognized that the second class, the porous, friable, loosely adherent deposit is the trouble maker in boilers by providing a region where ionic species may concentrate to initiate the final phases of failure under heat transfer such as hydroxide attack, hydrogen attack and metasomatosis. The first class is the trouble maker in valves and pumps.

The authors have committed themselves to the idea that the reacting contaminants are transported in, and react from, the soluble ionic states. Chemical thermodynamics then affords a powerful tool for evaluating the situation, despite the fact that, in general, it is not very useful in evaluating heterogeneous systems due to kinetic difficulties.

All thermodynamic calculations will be made at 25C. This is equivalent to the assumption that the changes in heat capacity for all reactions are zero at all temperatures (i.e., that only kinetics, not equilibria, are influenced by temperature.) Activity and concentration, as well as fugacity and pressure, will be used interchangeably for the very dilute solutions under consideration.

## Contaminants and Their Forms

*Iron*

Disregarding for the moment how the trivalent state is reached, a solution saturated with respect to trivalent iron will contain at least the ions $Fe^{+++}$, $Fe(OH)^{++}$, $Fe(OH)^{+}_{2}$ and solid $Fe(OH)_3$ together with its hydrates. Furtherfore, it probably is safe to assume that in a practical operating system the water is indeed saturated with trivalent iron, since the bivalent solubility exceeds the trivalent solubility by a large factor while the absolute values of both are extremely small, as will be shown later.

Equations governing the equilibrium concentrations of the trivalent iron ions are:

1. $Fe^{+++} + 3H_2O = Fe(OH)_3 + 3H^+$
   $\Delta F^\circ = +6600$ calories/gram mol
2. $Fe(OH)^{++} + 2H_2O = Fe(OH)_3 + 2H^+$
   $\Delta F^\circ = +3290$ calories/gram mol
3. $Fe(OH)^{+}_{2} + H_2O = Fe(OH)_3 + H^+$
   $\Delta F^\circ = -3110$ calories/gram mol
4. $\Delta F^\circ = -RT \ln K$

The equations have been written in terms of hydrogen ion rather than hydroxyl ion to emphasize the amphoteric nature of the soluble forms and to avoid the formal use of the water ion product constant. Symbols used in these and other equations are listed in a special section at the end of the article.

Solving these equations, it is found that the saturated equilibrium concentrations of the various trivalent iron ions as functions of the hydrogen ion concentration are:

5. $[Fe^{+++}] = [H^+]^3 \times 10^{4.84}$
6. $[Fe(OH)^{++}] = [H^+]^2 \times 10^{2.41}$
7. $[Fe(OH)^{+}_{2}] = [H^+] \times 10^{-0.28}$

A plot of the equilibrium trivalent iron ion concentrations is shown in Figure 1. Free energy data have been taken from Latimer.[1]

Figure 1 shows that essentially all of the soluble trivalent iron, at hydrogen ion

* Chemical engineer, Pacific Gas and Electric Company, San Francisco, California.
** Senior chemical engineer, Pacific Gas and Electric Company, San Francisco, California.

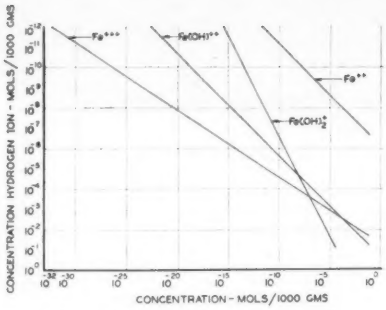


Figure 1—Solubility of iron ions in water.

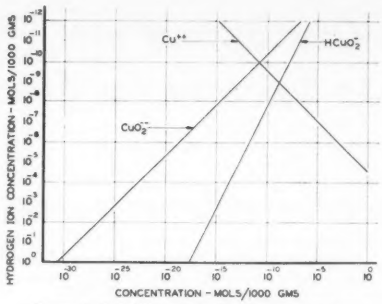


Figure 2—Solubility of the bivalent copper ions.

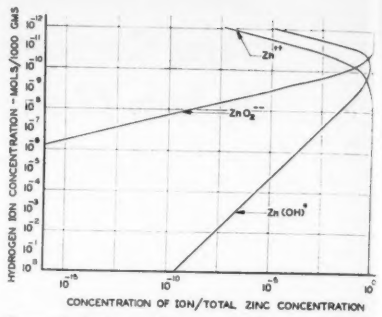


Figure 3—Ratio of the concentrations of bivalent zinc ions in water.

concentrations usually considered in steam generating stations, is in the form $Fe(OH)_2^+$. Also this solubility is very limited. It should be realized that the $Fe(OH)_3$ could be at any concentration level, even a slurry, without altering the results.

In the more alkaline environments the ferrite ion $FeO_2^-$ becomes important. The formation of this ion might be explained as the ionic neutralization of the hydrogen in $Fe(OH)_2^+$ by hydroxyl. This becomes plausible when one recalls that the mineral lepidocrocite, with the empirical formula $FeHO_2$ is a hydrogen bonded structure.[2]

Ferrite ion could, of course, be the active species, but thermodynamically there is very little to gain by considering this additional complexity. It is preferable here to base consideration of trivalent iron on the form $Fe(OH)_2^+$ alone and leave the possible transition through ferrite to kinetics.

No evidence is available that any bivalent iron ion except the simple ferrous ion is important in water solution.

Equations governing the saturated equilibrium concentrations of ferrous iron ion are:

8. $Fe^{++} + 2H_2O = Fe(OH)_2 + 2H^+$

$\Delta F^\circ = +18110$ calories/gram mol

9. $\Delta F^\circ = -RT1nK$

Solving these equations, it is found that the saturated equilibrium concentration of the ferrous ion as a function of the hydrogen ion concentration is:

10. $[Fe^{++}] = [H^+]^2 \times 10^{13.3}$

The solubility of ferrous ion is shown on Figure 1 for comparison with the trivalent iron ion solubilities.

*Copper*

Copper in the deposits in operating systems occurs most commonly in two valence states: metallic, or zero, and bivalent. Under some conditions monovalent copper is found. Since this ion is unstable with respect to auto oxidation-reduction to bivalent and metallic copper, it is thought unlikely that the monovalent ion plays any significant role in deposition from solution except as an intermediate.

Copper solubility is considerably greater than is trivalent iron solubility. Nevertheless, the same technique is used in estimating the solubility of the various bivalent ions by computing their equilibrium with cupric hydroxide, $Cu(OH)_2$. By a simple calculation it can be shown that with ammonia present to the extent of a few parts per million, cupric-ammonium complex ion formation is not a significant factor in the equilibria.

The bivalent copper ions considered are $Cu^{++}$, $HCuO_2^-$, and $CuO_2^=$. Their saturated equilibrium concentrations are shown in Figure 2.

The equations governing the equilibrium concentrations of the bivalent copper ions are:

11. $Cu^{++} + 2H_2O = Cu(OH)_2 + 2H^+$

$\Delta F^\circ = +12550$ calories/gram mol

12. $HCuO_2^- + H^+ = Cu(OH)_2$

$\Delta F^\circ = -23980$ calories/gram mol

13. $CuO_2^= + 2H^+ = Cu(OH)_2$

$\Delta F^\circ = -41800$ calories/gram mol

14. $\Delta F^\circ = -RT1nK$

Solving these equations, it is found that the saturated equilibrium concentrations of the various bivalent copper ions as functions of the hydrogen ion concentrations are:

15. $[Cu^{++}] = [H^+]^2 \times 10^{9.2}$

16. $[HCuO_2^-] = [H^+]^{-1} \times 10^{-17.6}$

17. $[CuO_2^=] = [H^+]^{-2} \times {}^{-30.6}$

The cupric hydroxide concentration could be at any level, even a slurry, as was pointed out for the similar situation for ferric hydroxide, without changing the results.

It is seen that the bivalent copper solubility and ion forms depend strongly upon the conditions. It cannot be said, as it could for example in the case of trivalent iron, that the soluble copper exists predominantly in a single form.

*Zinc*

The chemistry of zinc in both water and water-formed deposits is that of the bivalent form. However, the calculation of the ion forms and concentrations cannot be approached as it was for iron and copper because the hydroxide is too soluble. This means the absolute concentrations of the contaminating zinc ions cannot be fixed, but only the ratio of the various bivalent zinc ion concentrations to the total zinc concentration. These ratios are shown in Figure 3.

The zinc ions considered are $Zn^{++}$, $Zn(OH)^+$, and $ZnO_2^=$. A simple calculation shows that with ammonia present in the order of a fewer parts per million the bivalent zinc-ammonium complex ion is not a factor in the equilibrium.

The equation describing the equilibrium concentrations are:

18. $Zn^{++} + H_2O = Zn(OH)^+ + H^+$

$\Delta F^\circ = +13074$ calories/gram mol

19. $Zn^{++} + 2H_2O = ZnO_2^= + 4H^+$

$\Delta F^\circ = +55534$ calories/gram mol

20. $[Zn^{++}] + [Zn(OH)^+] + [ZnO_2^=] = (Zn)$

$(Zn)$ = Total zinc concentration

21. $\Delta F^\circ = -RT1nK$

Solving the equations gives:

22. $\dfrac{(Zn)}{[Zn^{++}]} = 1 + [H^+]^{-1} \times 10^{-9.58} + [H^+]^{-4} \times 10^{-40.7}$

23. $\dfrac{(Zn)}{[Zn(OH)^+]} = 1 + [H^+] \times 10^{9.58} + [H^+]^{-3} \times 10^{-31.12}$

24. $\dfrac{(Zn)}{[ZnO_2^=]} = + [H^+]^4 \times 10^{40.7} + [H^+]^3 \times 10^{31.12}$

There are, of course, other constituents found in the deposits but with iron, copper and zinc compounds usually accounting for well over 90 percent of the material, the ions considered together with the bivalent nickel ion completes the list under study.

**The Reactions of Copper, Iron and Zinc**

It should be emphasized at this point that what has been set forth previously is based upon the equilibrium between the species of an element in a given valence state. In general, however, equilibrium conditions do not exist in a feedwater system or boiler. This fact can be simply and convincingly demonstrated by measuring the oxidation-reduction potential of a feedwater stream with an inert electrode such as platinum.

*Oxidation of Bivalent Iron by Copper*

In the consideration of these reactions it is convenient to evaluate the driving potential for the conditions existing. For the ionic reactions postulated, this prob-

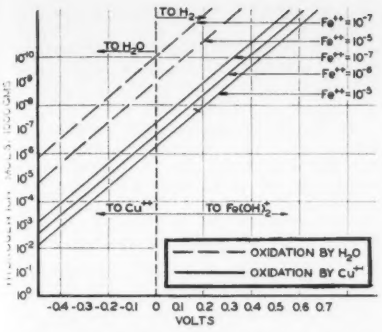


Figure 4—Potential for oxidation of bivalent iron.

ably is safe enough even though some reactants or products may be solid phases.

The driving potential will be given by the equation:

$$25.\quad E = \frac{RT}{n}[1nK - 1nQ]$$

where Q has the same form as the equilibrium constant but applies to the actual, rather than to the equilibrium, state.

The equations to be considered are:

$$26.\quad 2Fe^{++} + Cu^{++} + 4H_2O = 2Fe(OH)^+_2 + Cu + 4H^+ \qquad \log K = -28.9$$

$$27.\quad 2Fe^{++} + HCuO_2^- + 2H_2O = 2Fe(OH)_2^+ + Cu + H^+ \qquad \log K = -2.2$$

$$28.\quad 2Fe^{++} + CuO_2^{=} + 2H_2O = 2Fe(OH)_2^+ + Cu \qquad \log K = 10.9$$

together with six similar equations for $Fe(OH)^{++}$ and $Fe^{+++}$. However, the manner in which the ionic concentrations of trivalent iron and bivalent copper are fixed, by assuming equilibrium with their hydroxides, makes it necessary to consider only one equation as all give the same potential.

Using equations 7, 15, and 26 the following relationship is obtained for the oxidation potentials due to the various copper ions:

$$29.\quad E = -0.448 - 0.05916 \log \frac{[H^+]^2}{[Fe^{++}]}$$

The values of the driving potential are shown in Figure 4 as functions of the hydrogen ion and ferrous iron concentrations. A positive sign for the potential indicates the reaction tends to go as written.

The potentials indicated in Figure 4 might be considered quite respectable for the lower hydrogen ion concentrations when it is recalled that the potential of normal acid to zinc is only 0.763 volts. It seems reasonable to speculate that the reaction of bivalent iron and copper might be rapid.

It might be well to reiterate that the bivalent copper concentration is not strictly limited, the reservoir being the cupric hydroxide or hydrated copper oxide which can be at any level, even a slurry. This copper is perfectly capable of reverting to the soluble bivalent forms for further reaction with bivalent iron.

If one accepts the mechanisms postulated, the inevitable conclusion reached is that if the atomic ratio of bivalent copper to bivalent iron contamination is substantially more than one-half, essentially all of the iron will be converted first to the trivalent $Fe(OH)_2^+$ and, if no other reaction intervenes, finally to the trivalent $Fe(OH)_3$ solid phase.

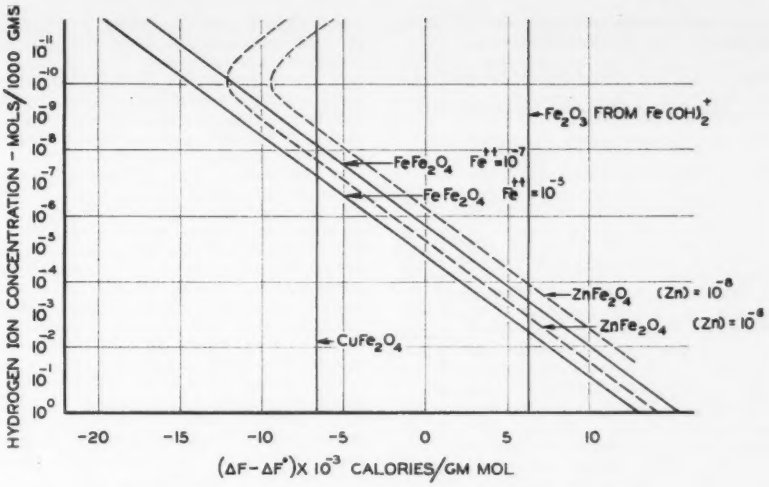


Figure 5—Driving energy in magnetite and substituted magnetite formation.

This then provides a mechanism for the deposition of metallic copper for a normally operating system without resort to abnormal phenomena such as overheating, reduction by hydrogen, etc (see Equations 26, 27, and 28). It also furnishes an explanation for the fact that copper is seldom, if ever, found plated directly on steel, as it would be if metallic iron had caused the reduction. As observed, the copper is plated over oxides or on particles of oxide.

*The Reactions of Soluble Trivalent Iron*

Having accounted for the formation of the soluble trivalent iron ions it is now possible to examine the way in which they enter into the deposition reactions. Trivalent iron is found almost exclusively in magnetite, substituted spinel structures in which some of the ferrous iron of magnetite has been replaced by another bivalent metal, and hematite or its hydrates.

Attention will be directed primarily to interaction and reaction with ferrous iron, bivalent copper and bivalent zinc. The reactions considered are:

$$30.\quad 2Fe(OH)_2^+ + Fe^{++} = FeFe_2O_4 + 4H^+ \qquad \Delta F^\circ = -10000 \text{ calories/gram mol}$$

$$31.\quad 2Fe(OH)_2^+ + Cu^{++} = CuFe_2O_4 + 4H^+ \qquad \Delta F^\circ = -19100 \text{ calories/gram mol}$$

$$32.\quad 2Fe(OH)_2^+ + Zn^{++} = ZnFe_2O_4 + 4H^+ \qquad \Delta F^\circ = -18800 \text{ calories/gram mol}$$

$$33.\quad 2Fe(OH)_2^+ = Fe_2O_3 + 2H^+ + H_2O \qquad \Delta F^\circ = -21390 \text{ calories/gram mol}$$

Since there is no obvious electron transfer in these reactions, the electrical potential is not convenient to represent the driving force; thus a slightly different approach is taken. The equation:

$$34.\quad \Delta F = -RT1n\frac{K}{Q}$$

gives the free energy of any reaction. With rearrangement and substitution this gives:

$$35.\quad \Delta F - \Delta F^\circ = RT1nQ$$

where $\Delta F - \Delta F^\circ$ is the deviation from equilibrium and represents the driving force for the reaction. Being ionic reactions they will go spontaneously if $\Delta F - \Delta F^\circ$ is negative.

The values of $\Delta F - \Delta F^\circ$ as functions of hydrogen ion concentration are shown on Figure 5. With respect to Figure 5 it will be noted that the formation of hematite from trivalent iron *in solution* does not take place. Of additional interest are the curves for the zinc substituted magnetite; the minimum in the curves may explain the reported fact[3] that zinc-containing deposits are more prone to form in low alkalinity boiler water.

Mention should be made that nickel, cobalt, cadmium and possibly manganese also would form substituted magnetites under conditions in a feed-water system or boiler. The authors personally have found reasonably well-authenticated cases of copper and zinc substitution only.

These reactions are sufficient to account for the form and composition of the smooth, dense, adherent deposits and the dense powders and sludges. The former arises from crystal formation from solution in contact with the walls; the latter from intra-solution precipitation.

*The Reactions of the Hydroxides*

It has been stated previously that essentially all the bivalent iron contamination will be converted first to the trivalent $Fe(OH)_2^+$ and, if no other reaction intervenes, finally to the trivalet $Fe(OH)_3$ solid phase if the atomic ratio of bivalent copper to bivalent iron is substantially more than one-half.

It has now been shown the other reactions (reactions 30, 31 and 32) do indeed intervene and at least a portion of the $Fe(OH)_2^+$ is precipitated as magnetite and substituted magnetites. A compet-

ing precipitation reaction for the very limitedly soluble $Fe(OH)_2^+$ is:

36. $Fe(OH)_2^+ + H_2O = Fe(OH)_3\downarrow + H^+$

$\Delta F° = -3100$ calories/gram mol

followed by the thermal dehydration:

37. $2Fe(OH)_3 = Fe_2O_3 + 3H_2O$

$\Delta F° = -15170$ calories/gram mol

This is a reaction that cannot be treated under the assumptions made with respect to activities and specific heats. It is a well-known laboratory reaction perfectly capable of hematite formation after the ferric hydroxide state is reached even though, as shown, it does not occur from solution. It will not be considered further here except to say that it can account for the loosely adherent porous deposits and porous sludges—the former if dehydrated in contact with a wall, and the latter if dehydrated within the solution.

Similar reactions can account for the usually moderate percentages of copper oxides found in the deposits. This however does not seem to be very important. If a surplus of copper reaches the boiler, it would seem that sufficient ferrous iron always reaches the water by diffusion from the steel-deposit interface to essentially complete the copper reduction. Thus the metal is the principal form of surplus copper.

*Oxidation of Bivalent Iron by Water*

It is well known that iron and water alone will form magnetite without the intervention of copper or other oxidizing agent. It might then be instructive to apply the principles used and compare the results with the copper potentials shown on Figure 4.

Consider the reaction:

38. $Fe^{++} + 2H_2O = Fe(OH)_2^+ + \frac{1}{2}H_2 + H^+$

$\Delta F° = +27480$ calories/gram mol

$\log K = -20.2$

Assuming a hydrogen partial pressure of $10^{-10}$ atmospheres, which corresponds to something like 5 - 10 parts per billion of hydrogen at 2000 psig, the potential for this reaction becomes:

39. $E = -0.765 - 0.05916 \frac{[H^+]^2}{[Fe^{++}]}$

This driving potential is shown on Figure 4 as a function of hydrogen ion concentration and the bivalent iron concentration. One will note that, though this reaction will proceed at a hydrogen ion concentration less than about $10^{-9.5}$ the driving potential is several orders of magnitude less than the driving potential with the copper intervention.

## Summary and Application

A set of reactions have been presented which form a framework comprehensive enough, with one exception, to qualitatively account for the form and composition of all the deposits observed in the water portions of the cycles of 43 boilers operating at pressures above 1300 pounds per square inch. The exception is the presence of one percent or so of metallic iron associated with magnetite in some of the deposits. Nothing in the postulated mechanisms can account for this.

It might be well to review once again the various sets of reactions. In so doing, it is noted that:

1. The reactions 26, 27 and 28 between ferrous iron and bivalent copper account for the formation of soluble trivalent iron and metallic copper in a straightforward manner.

2. The reactions 30, 31 and 32 (note: 33 does *not* go) of soluble trivalent iron and bivalent iron, copper, zinc or nickel form magnetite and substituted magnetite by crystal formation from solution. From these reactions it is possible to obtain deposit classes A and C-1 enumerated earlier (i.e., dense, brittle, tightly adherent deposits on the walls and dense non-adherent sludge if precipitated in the bulk solution.)

The dense, tightly adherent deposit, class A, presents a dimensional problem in equipment such as pumps or valve cages. Both classes, however, have been found relatively harmless under heat transfer.

3. With a substantial excess of bivalent copper, the solubility limit of $Fe(OH)_2^+$ is quickly reached and the precipitation of ferric hydroxide, Equation 36, can compete successfully with the magnetite precipitation reactions, Equations 30, 31 and 32.

On dehydration in the solution, Equation 37, ferric hydroxide forms non-adherent porous sludges, class C-2. When in contact with a wall, it forms a loosely adherent porous deposit, class B, which then becomes the site of disastrous concentration under heat transfer.

To illustrate these points the following plant conditions are cited:

1. High iron, 50 ppb; Low copper, 10 ppb; Low ratio 0.2
2. High iron, 60 ppb; High copper, 30 ppb; Moderate ratio 0.5
3. Low iron, 10 ppb; High copper, 30 ppb; High ratio 3.0

In the plant examples, reference is made to the total iron and copper as determined analytically with the copper to iron ratios based on these determinations. This means that the numbers quoted are not on the bivalent basis as used throughout the development. This is an analytical compromise, not one of principle.

Plant 1, with ten years' operation, has had essentially a dense, tightly adherent magnetite deposit, and dense non-adherent magnetite sludge with granular copper or copper plated on iron oxide particles. The iron excess is finally precipitated as a non-adherent iron phosphate sludge in the boiler.

Plant 2, with eight years' operation, has had essentially dense, tightly adherent magnetite and substituted magnetite deposits, dense non-adherent magnetite and substituted magnetite sludge and granular copper or copper plated on iron oxide particles.

Plant 3, with three years' operation, has had essentially dense, tightly adherent magnetite and substituted magnetite, loosely adherent hematite, magnetite, substituted magnetite, copper foil and granular copper or copper plated on iron oxide particles.

Only Plant 3 has been adversely affected, and it will be noted that the loosely-adherent hematite, class B, which comes from a substantial excess of bivalent copper over iron is the real distinction in the deposits of this plant. Also, it is the ratio of copper to iron, not the absolute levels, that is the real distinction in the water of this plant.

Thus it would appear that the authors' principal thesis has been established.

## Conclusion

It has been shown that mechanisms based upon the thermodynamics of the soluble ions from the corrosion of the materials of construction can qualitatively account for both the form and composition of the deposits from high purity water in large steam generating stations.

So far as trouble from deposits is concerned, the ratio of copper to iron seems more important than the absolute concentrations of either. Small variations in the concentration of other ions do not seem important.

## List of Symbols

$\Delta F°$—Free energy of reaction when all reacting substances are at unit activity. Calories/gram mol.

$\Delta F$—Free energy of reaction for actual conditions. Calories/gram mol.

R—Gas constant—Calories/gram mol °K.

T—Temperature—°K.

[ ]—Concentration—gram mols/1000 grams $H_2O$.

[ ]—Pressure—atmospheres.

K—Equilibrium Constant.

Q—Equilibrium Constant form for actual conditions.

( )—Total concentration—gram mols/1000 grams $H_2O$.

E—Oxidation potentials—volts.

n—Number of electrons transferred in reaction as written.

ppb—Parts per billion by weight.

ln—Naperian logarithm.

log—Logarithm to base ten.

## References

1. W. M. Latimer. Oxidation Potentials, 2nd., Ed., Prentice Hall, 1952.
2. F. J. Ewing. *J. Chem. Phys.*, **3**, 203 (1935).
3. F. U. Neat. ASME Paper No. 55-S-38.

## Appendix

The iron-containing spinel type minerals seem very important in the deposits formed from the high purity water in large steam generating stations. These minerals are cubic crystals having eight formula molecules in their crystal pattern and the Schoenflies space group $O_h^7$.

In mixtures their identification is extremely difficult. Practically the only tools available are the X-ray diffraction techniques. It is not surprising, then, that they are seldom reported on a routine examination. The most likely ones, $ZnFe_2O_4$, $FeFe_2O_4$ and $CuFe_2O_4$ are almost identical in their crystal spacing.

The parent compounds $H_2Fe_2O_4$, lepidocrocite and goethite, are not spinel type minerals and will be recognized and reported as a hydrated ferric oxide.

Some of these iron-containing minerals and their crystal spacing are tabulated for comparison.

| Formula | Spacing Å |
|---|---|
| Iron In Anion | |
| $NiFe_2O_4$ | 8.35 |
| $MgFe_2O_4$ | 8.36 |
| $CoFe_2O_4$ | 8.38 |
| $ZnFe_2O_4$ | 8.40 |
| $FeFe_2O_4$ Magnetite | 8.40 |
| $CuFe_2O_4$ | 8.44 |

| Formula | Spacing A |
|---|---|
| Iron In Anion | |
| $TiFe_2O_4$ | 8.50 |
| $MnFe_2O_4$ | 8.54 |
| $CdFe_2O_4$ | 8.67 |
| Iron As Cation | |
| $FeAl_2O_4$ | 8.10 |
| $FeCr_2O_4$ | 8.35 |
| $FeV_2O_4$ | 8.47 |

## DISCUSSION

**Comment by Robert D. Misch, Argonne National Laboratory, Lemont, Illinois:**

The thermodynamic calculations of this paper should be compared with the data of Pourbaix* who has presented a potential—pH diagram for the iron-water and possibly for the copper-water system.

**Discussion By B. A. Kronmiller, The Flox Co., Alameda, Calif.:**

The authors have presented a concept of iron oxide deposit formation from high purity water systems with a degree of thoroughness and lucidity seldom found in this field. Their orderly utilization of fundamental equilibria and thermodynamic relationships to arrive at a positive mechanism for producing various deposit formations displays a combined knowledge of plant operation, laboratory technique and—perhaps most important—the ability to apply abstract chemical relationships to a highly practical problem.

The authors' principal thesis may be, perhaps, somewhat more all-inclusive than desirable in view of their stated experience. It is this writer's opinion that a modification of this thesis can be justly derived from considerable field and laboratory experience which will materially broaden the applicability of their information and prevent the possible arrival at erroneous conclusions in some instances.

The substantiation of their inclusive thesis appears to be well established by their excellent interpretation and application of the equilibrium reactions for the several materials of construction. The authors have, however, preferred to limit their discussion to a thermodynamic consideration rather than becoming involved in the kinetics also applicable. This limitation may possibly act to restrict the accuracy of their statement of theory or all-inclusive thesis but not the facts from which it was derived.

Through a consideration of ferrous iron solubility alone as the initial product of corrosion (shown in Figure 1)—in the range of 0.01 to 1.0 ppm range established by the authors and generally not in excess of 0.1 ppm—field and experimental laboratory boiler experience shows that disastrous deposits formation of Type B can be attained simply through variation of heat transfer rates. The higher rates generally produce denser and heavier deposits. Copper contaminants in the adverse ratios proposed by the authors or substituted magnetites do not appear to be involved. Iron contamination in this range, however, without adverse heat transfer rates, does not appear to present a problem, in this writer's experience, unless copper is present in considerable quantity—possibly in the troublesome ratio suggested by the authors.

Application of treatment programs designed primarily for reduction of iron pick-up in the feedwater system have been quite successful in reducing boiler deposit problems even though the absolute level of iron contamination was not appreciably altered. This anomaly possibly may be explained by the iron to copper ratio effects proposed by the authors, since it is well established that elevation of the pH of high purity feedwater by the addition of volatile, alkaline materials, such as morpholine, in combination with a reduction in oxygen content, reduces the copper contamination in many instances. A possible mechanism for this is shown in Figure 2. It is quite feasible to agree, then, that the copper to iron ratio upset in this manner is considerably more important to the resulting improvement of boiler conditions than the absolute levels of either contaminant if the original deposition resulted from adverse ratios.

If, however, the original problem, in the absence of adverse ratios, were due to iron deposition resulting from heat transfer rates, then a reduction in ferrous iron solubility and the absolute level of this contaminant will be of material importance to a logical solution.

It is interesting to note here that the very dense, tenaciously adherent deposits of magnetite and/or substituted magnetities listed as Type A have not successfully been produced in experimental boiler studies, to this writer's knowledge, where no copper was present except under extremely high rates of heat transfer beyond any normally expected range. This also tends to support the authors' equilibria data. It would appear that further experimental boiler studies could establish the validity of these equilibria and their limitations quite readily.

For the record, it would be interesting to know from which sampling point or points the authors feel the most significant analyses or iron and copper come. Some discussion of sampling and analytical techniques employed in arriving at reliable and significant values in the ranges indicated also might be of major interest.

**Discussions By W. A. Keilbaugh, The Babcock and Wilcox Co., Research Center, Alliance, Ohio**

The authors are certainly to be commended on an approach to deposition within boiler circuits which is, as far as we know, quite original and which undoubtedly will serve as a stimulus to future thinking in this area.

It is true, at least on a relative basis, that "problems relating to corrosion and deposition both in the feedwater and boiler circuits of large power plants have become more acute" as more and more high pressure units go into service. Advances in make-up water treatment, the introduction of more efficient boiler steam separating and washing equipment, and increased technological proficiency on the part of plant operators have been responsible for a vast reduction in other boiler operating problems.

The postulation that "satisfactory" deposition, as contrasted with deposition that leads to failure, depends essentially upon the ratio of copper to iron in the water and not upon the absolute levels of either does not appear to correlate too well with the experience of other utilities of our acquaintance. We know of no instances in which improvements in boiler water-side conditons, from the standpoints of depositon and/or corrosion, were not evident if a reduction of total contamination entering the boiler were made.

A case in point is a very recent contact with the chief chemist of an eastern utility who has been feeding morpholine to one of his units in an effort to reduce feedwater contamination by condensate return and pre-boiler system corrosion products. His experience can be briefly summed up as follows:

1. There has been a very great reduction in the amount of water side deposition of both iron and copper in this unit.
2. Before the use of morpholine the deposits were predominately iron oxides with lesser (on the order 15 percent) amounts of copper.
3. After the use of morpholine the deposits consisted of approximately 65 percent copper with correspondingly less iron.

It is believed that this example is reasonably representative of the experiences of others where attempts have been made through properly controlled condensate treatments to reduce boiler feedwater contamination.

During the past few years it has been evident from both pilot plant and field experiences that boiler feedwater corrosion product contamination is transported in both soluble and insoluble forms, the amounts of both apparently varying not only with plant configuration and water conditions but also changing according to such variables as load fluctuations. Although soluble forms cannot in any way be minimized, it is believed that deposition within the boiler can result directly from the contaminant solid form without a transition through some soluble state.

Attempts to definitely distinguish the relative amounts of soluble and insoluble matter have not, to our knowledge, been conspicuously successful. Ultrafine pore size filters and ion exchange bed filtering have not proven that they can furnish the ultimate answer.

With these items in mind, this discusser's company is currently recommending the use of commercially available semi-continuous evaporator samplers in place of spot sampling, filtering or ion exchange sampling. It is felt that better long term representations of contaminant levels can be procured in this way. This also provides a larger solids sample, less subject to error through introduction of small amounts of extraneous contamination or variances in analytical techniques.

In connection with the analytical work, a precautionary note is in order. It has been found in our laboratory in the analysis for iron in condensates and boiler feedwaters, that it is necessary to digest the samples by a strong digestion procedure (perchloric acid is used in our laboratory) in order to be completely certain that all insoluble iron is properly solutioned prior to proceeding with either the widely used ortho or batho penanthroline spectrophotometric analyses.

Of particular interest is the authors' postulation of the oxidation of bivalent iron by some form of copper. Closely controlled pilot plant work in our laboratory tends to substantiate this postulation. In this work it has been indicated that some ferrous iron can be oxidized

* *J. Electrochem. Soc.*, **98**, 57, 65, 101 (1951); *CITCE Proceedings*, 1950, 1951, 1954.

to the ferric form, with the production of metallic copper, and in the essential absence of oxygen and hydrogen, by the presence in the boiler water of a soluble form of copper. The oxidation was not discernible under otherwise identical conditions in the absence of copper.

The problems associated with this subject will continue to be of utmost interest and the authors' work can certainly be considered one more step in aiding a better understanding of the mechanisms involved.

**Replies By E. S. Johnson and H. Kehmna**

We wish to thank Messrs. Kronmiller and Keilbaugh for discussion of our efforts. Both discussers have mentioned the effect of feedwater treatment with alkaline materials. This lies outside the portion of the corrosion, transport and deposition mechanisms we chose to consider. It will be recognized, however, that our thesis is part of a much larger proposition, namely, that a substantial excess of any oxidizing agent will lead to similar results. The remarks then with respect to feedwater treatment with alkaline materials become doubly pertinent in that the materials not only influence the contamination but the rates of reaction between the contaminants.

In answer to Mr. Kronmiller, at the present time we have no basis for preferring one sampling point over another. We never make copper and iron determinations on a routine basis, but rather set up a task force to survey a cycle as nearly "all at once" as is possible. To do this we use all the sample points available and make several hundred grab sample determinations to use in establishing a pattern. If one point were to be chosen, it would be after feedwater collection is complete but before the high pressure feedpumps; this point would of course not be the same in all cycles and could conceivably not exist in some cycles.

The matter of strong digestion of samples brought up by Mr. Keilbaugh is a point well made. In our laboratories we use a mixture of nitric and hydrochloric acids. Radically different results are obtained without the oxidizing mixture.

In closing we wish to say that we are well aware of the importance of kinetics in this manner. Very real difficulties, however, caused us to prefer to avoid the subject. Should our efforts incite someone to look into the kinetics of the reactions we would feel well repaid.

Part 2—Atmospheric Corrosion of Ten Structural Steels

# Corrosion of Metals in Tropical Environments*

By C. R. SOUTHWELL*, B. W. FORGESON* and A. L. ALEXANDER*


## Abstract

Results are reported of 8-year exposure tests made to determine the corrosion characteristics of ten structural steels exposed to seashore and inland environments in the Panama Canal Zone. These corrosion rates are compared with existing data for the same materials in temperate zones.

Data reported include a summary of individual analyses of air samples obtained at atmospheric test sites, and extensive weight-loss and pitting data for the ten steels at 1, 2, 4 and 8-year exposure intervals. Numerous time-corrosion curves in tropical marine and tropical inland exposures are given for the steels.

Considerable attention is given to the effect of low-alloy additions on mild carbon steel. It was found that the corrosion of copper steel in the two tropical atmospheres was only 13 percent and 14 percent less than that of the unalloyed mild steel. The 2 percent and 5 percent nickel steels were very effective in resisting corrosion as was nickel steel. The four proprietary low-alloy steels tested displayed good corrosion resistance to tropical atmospheric corrosion. 2.2.2


## Introduction

AN EXTENSIVE investigation has been in progress since 1946 in the Panama Canal Zone to study the corrosion rates and characteristics of 50 different metals and alloys exposed to five natural tropical environments: marine and inland atmospheres, fresh water immersion, and continuous and mean tide sea water exposure.

As a result of an earlier study,[1] it was considered necessary to make periodic measurements over a period of 16 years in order to predict with considerable accuracy the useful life in the tropics of the metals included in the study. Ten replicate panels of each metal were exposed in each environment so that two panels from each location could be removed after one, two, four, eight and sixteen years. The eight-year specimens were removed in the summer of 1955, thus providing the fourth point for time-corrosion curves. An earlier report,[2] incorporating the first of the eight-year data, described the methods and procedures employed and devoted special attention to the corrosion rates of five unalloyed metals and a structural steel in the five natural tropical environments.

Of the 50 metals and alloys included in the Canal Zone study, ten are in the category of commercial-type structural steels. Investigations of the corrosion rate of similar structural steels in rural, industrial, and marine atmospheres in the temperate zone by Larrabee,[3, 4] Hudson and Stanners,[6] and others have created considerable interest in their behavior. The now well-known increase in resistance to corrosion in the atmosphere by the addition of very small amounts of alloying constituents to carbon steel has been utilized by steel producers throughout the world. The present paper attempts to widen the scope of knowledge of corrosion of structural steels in natural environments by presenting results for ten of these metals exposed for eight years to the corrosive marine and inland atmospheres of the tropics in the Panama Canal Zone.

## Test Conditions

### *Exposure Environments*

The atmosphere at each of the test sites was sampled during the period from May 1947 to November 1950, and chemical constituents of significance to corrosion are shown in Table 1. Samples were taken continuously by aspiration methods using distilled water as an absorbent to collect air-borne material. Analysis of this absorbent water was made three times a year representing periods from January to April inclusive (dry season), May to August inclusive (wet season), and September to December inclusive (wet season).

The Canal Zone, fortunately, is one of the few tropical areas in the world for which accurate and long-term weather information is available, having been collected by the Panama Canal Department of Meteography and Hydrography. Data showing monthly variations in temperature, humidity, rainfall, wind, and sunshine for an average year based on a minimum record of 20 years were published in an earlier paper[2] in this series.

### *Metals and Methods*

Of the ten structural steels evaluated for corrosion resistance to the tropical atmospheres, four were proprietary high-strength low-alloy types; one was a 2 percent nickel boiler steel, RR Specification 3-A; one was SAE-2515, a 5 percent nickel steel; two were high-tensile chromium steels, a proprietary of 3 percent chromium content and an AISI Type 501D of 5 percent chromium content; and two were Federal Specification QQ-S741 low-carbon steels, one copper-bearing and the other unalloyed. Compositions of these steels and those from Reference 3 with which comparisons will be made are given in Table 2.

The samples of the steel exposed in tropical environments were 4 x 8 x 1/16 inch panels, with the exception of unalloyed structural steel. That sample was ⅛ inch thick rather than 1/16 inch because of the higher rate of corrosion anticipated.

Samples were prepared for exposure by pickling for ten minutes in 10 percent $H_2SO_4$ at 170 F, after which they were weighed and measured. The panels were then exposed to the atmosphere at Miraflores and Cristobal, Canal Zone, mounted on stainless steel racks with the specimens held at an angle of 30 degrees from the horizontal.

The exposure area at Miraflores represents an inland tropical condition without jungle shade, as the area is completely cleared. At this location, which is approximately five miles inland from the Pacific entrance of the Canal, the prevailing winds are from the inland side (north). Racks are on the ground and face south. The Cristobal test area is in a tropical marine atmosphere, as the site is located only 300 feet from the Caribbean seacoast, and the prevailing winds are from the ocean. The racks are situated on the roof of the Washington Hotel at an elevation of 55 feet above sea level and face north toward the sea.

Upon removal, samples were chemically cleaned by immersion in 10 percent $H_2SO_4$ with 1 percent quinoline ethiodide inhibitor. Additional mechanical cleaning was employed as required. Cleaned samples were measured and weighed for determination of pitting, dimensional changes, and weight loss. A more complete description of the test procedure is given in Reference 2.

## Corrosion Results

The visual and measured corrosion information for the ten structural steels included in this report is summarized in Table 3. Average reduction in thickness rather than average penetration was used because of different rates of penetration on the groundward and skyward side of the panels (Figure 1). This difference also affects the pitting factor, which, although inexact because of the difference in groundward and skyward side corrosion, still is considered useful for evaluating corrosion damage on steel specimens.

Evaluation of the data presented in Table 3 indicates that for Canal Zone atmospheric environments the AISI Type 501D 5 percent chromium steel was the most corrosion resistant of the group tested. However, the SAE-2515 (5 percent nickel) and the RR Specification (2 percent nickel) steels were almost equally as resistant. The 2 percent nickel steel, considering its lower alloying cost, would seem to be a wise selection for atmospheric exposure in the tropics. The proprietary low-alloy steels could also compete on a cost basis, and in atmospheric corrosion resistance they are much superior to the low-carbon and copper-bearing steels.

## Relative Intensities of Atmospheric Corrosion

Obviously it would be helpful to establish factors, or coefficients, relating

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* U.S. Naval Research Laboratory, Washington, D.C.

**TABLE 1—Summary of Individual Analyses of Air Samples Obtained at the Atmospheric Test Sites**

| CONSTITUENT (Determined in mg per 100 cu. ft.) | CRISTOBAL TEST SITE | | | MIRAFLORES TEST SITE | | |
|---|---|---|---|---|---|---|
| | Maximum | Minimum | Average | Maximum | Minimum | Average |
| Total Dissolved Solids | 5.48 | 0.30 | 1.70 | 2.58 | 0.15 | 0.86 |
| Organic and Volatile Matter | 1.72 | 0.16 | 0.74 | 0.69 | 0.11 | 0.34 |
| Sulfate | 0.64 | 0.030 | 0.20 | 1.13 | 0.011 | 0.25 |
| Chloride | 0.42 | 0.035 | 0.23 | 0.16 | 0.013 | 0.055 |
| Nitrate | 0.11 | 0.00 | 0.031 | 0.12 | 0.00 | 0.040 |

**TABLE 2—Composition of Structural Steels Exposed in Tropical and Temperate Climates**

| Steel | Type | Specification | COMPOSITION (Percent) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | Mn | P | S | Si | Cr | Ni | Cu | Mo |
| A | Unalloyed low-carbon | QQ-S-741, Type II Grade A, Class 1 | 0.25 | 0.46 | 0.083 | 0.014 | 0.004 | 0.025 | 0.035 | 0.020 | .... |
| B* | Unalloyed low-carbon | | 0.16 | 0.42 | 0.013 | 0.021 | 0.01 | 0.01 | 0.02 | 0.02 | .... |
| C | Low-alloy | Proprietary Cu-Ni | 0.13 | 0.41 | 0.007 | 0.026 | 0.048 | .... | 1.70 | 0.90 | .... |
| D | Low-alloy | Proprietary Cu-Cr-Si | 0.12 | 0.41 | 0.084 | 0.026 | 0.50 | 0.60 | 0.63 | 0.43 | .... |
| E | Low-alloy | Proprietary Cu-Ni-Mn-Mo | 0.087 | 0.73 | 0.65 | 0.018 | 0.067 | 0.03 | 0.82 | 0.59 | 0.19 |
| F | Low-alloy | Proprietary Cr-Ni-Mn | 0.11 | 0.54 | 0.086 | 0.029 | 0.18 | 0.50 | 0.40 | 0.57 | .... |
| G* | Low-alloy | | 0.09 | 0.24 | 0.15 | 0.024 | 0.80 | 1.1 | 0.05 | 0.43 | .... |
| H* | Low-alloy | | 0.06 | 0.48 | 0.11 | 0.030 | 0.54 | 1.0 | 0.51 | 0.41 | .... |
| I* | Low-alloy | | 0.05 | 0.36 | 0.05 | 0.016 | 0.008 | 0.01 | 2.0 | 1.1 | .... |
| J* | Low-alloy | | 0.11 | 0.55 | 0.08 | 0.026 | 0.06 | 0.31 | 0.28 | 0.55 | .... |
| $K_1$* | Low-alloy | | 0.16 | 1.4 | 0.013 | 0.021 | 0.18 | 0.03 | 0.50 | 0.30 | .... |
| $K_2$* | Copper-bearing | | 0.27 | 0.48 | 0.024 | 0.036 | 0.009 | 0.12 | 0.01 | 0.21 | .... |
| L | Copper-bearing | QQ-S-741 Class 2 | 0.22 | 0.41 | 0.004 | 0.030 | 0.008 | 0.015 | 0.10 | 0.24 | .... |
| M | Nickel (2%) | RR-SPECS-3-A | 0.18 | 0.52 | 0.036 | 0.024 | 0.19 | 0.14 | 2.06 | 0.61 | .... |
| N | Nickel (5%) | SAE-2515 5% Ni Steel | 0.10 | 0.50 | 0.01 | 0.21 | 0.20 | 0.07 | 4.55 | 0.054 | 0.074 |
| O | Chromium (3%) | Max. 0.10% C Hot Rolled | 0.07 | 0.54 | 0.008 | 0.016 | 0.14 | 3.24 | 0.13 | 0.11 | 0.032 |
| P | Chromium (5%) | Co 1% AISI Type 501D | 0.12 | 0.58 | 0.020 | 0.014 | 0.32 | 5.20 | 0.060 | 0.036 | 0.41 |

* Exposed by Larrabee[3] in temperate climates.

corrosion rates in tropical atmospheres with those in similar environments in temperate zones. Larrabee[3,4] has done considerable work with steels of similar compositions at Kure Beach, N. C. It is significant that the two groups of low-alloy steels which should be quite similar in corrosion resistance because of their similar chemical compositions (steels C-$K_1$, Table 2) exhibit a marked difference in corrosion rates at the two marine sites (Figure 2). After eight years, the average extent of corrosion of the low-alloy steels at Cristobal is over twice that of similar low-alloy steels exposed at Kure Beach. Unalloyed low-carbon steel at Cristobal is over twice that of similar low-alloy steels exposed at Kure Beach. Unalloyed low-carbon steel at Cristobal (steel A, Table 2) showed approximately 60 percent increase in corrosion compared with a similar steel (steel B, Table 2) at Kure Beach.

It is assumed that the Kure Beach tests were made in the 800-foot lot. The Cristobal tests were made atop the Washington Hotel, located 300 feet from the edge of the water at an elevation of 55 feet. The panels were mounted on racks at a height slightly above a 3-foot parapet extending above the roof of the hotel.

In Figure 3 the results with unalloyed low-carbon steels and the four low-alloy steel exposed at Miraflores are compared with the results from the same metals exposed to the marine atmosphere at Cristobal. After eight years, the low-alloy steels at the inland site showed approximately 50 percent less corrosion than the same steels exposed at Cristobal.

By comparing the curves in Figures 2 and 3 it can be seen that the corrosion of the low-alloy steels, even in the clean tropical inland atmosphere,

**TABLE 3—Comprehensive Evaluation of Corrosion Damage for Ten Structural Steels Exposed to Tropical Atmospheres in the Panama Canal Zone**

| Steel | Exposure | Weight Loss (g/dm²) | | | | Average Reduction in Thickness (Mils)* | | | | Average 20 Deepest Pits (Mils)** | | | | Deepest Pit (Mils)** | | | | Pitting Factor*** | | | | Rank**** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 Yr | 2 Yr | 4 Yr | 8 Yr | 1 Yr | 2 Yr | 4 Yr | 8 Yr | 1 Yr | 2 Yr | 4 Yr | 8 Yr | 1 Yr | 2 Yr | 4 Yr | 8 Yr | 1 Yr | 2 Yr | 4 Yr | 8 Yr | |
| L | Marine | 4.34 | 7.07 | 9.10 | 17.45 | 4.4 | 7.1 | 9.2 | 17.6 | 10 | 11 | 8 | 32 | 15 | 26 | 12 | 66(P) | 7 | 7 | 3 | 8 | 5 |
| | Inland | 2.75 | 4.66 | 7.21 | 10.96 | 2.8 | 4.7 | 7.3 | 11.0 | 4 | 6 | 6 | 14 | 5 | 9 | 9 | 22 | 4 | 4 | 2 | 4 | |
| M | Marine | 3.07 | 3.92 | 5.05 | 7.48 | 3.1 | 4.0 | 5.1 | 7.5 | 13(5) | 6 | 10 | 11 | 14 | 10 | 11 | 21 | 9 | 5 | 4 | 6 | 2 |
| | Inland | 1.84 | 2.94 | 4.27 | 5.65 | 1.9 | 3.0 | 4.3 | 5.7 | | 4 | 9 | 11 | | 6 | 12 | 15 | 0 | 4 | 5 | 5 | |
| N | Marine | 2.67 | 3.63 | 4.57 | 7.07 | 2.7 | 3.7 | 4.6 | 7.1 | 10 (16) | 9 | 8 | 11 | 15 | 15 | 11 | 13 | 11 | 8 | 5 | 4 | 2 |
| | Inland | 1.98 | 2.55 | 4.21 | 5.31 | 2.0 | 2.6 | 4.2 | 5.4 | 5 (16) | 0 | 7 | 10 | 9 | 0 | 9 | 16 | 9 | 0 | 4 | 6 | |
| O | Marine | 3.93 | 4.97 | 6.01 | 9.03 | 4.0 | 5.0 | 6.1 | 9.1 | 12 | 12 | 14 | 18 | 17 | 30 | 26 | 63(P) | 9 | 12 | 9 | 14 | 4 |
| | Inland | 2.06 | 2.58 | 2.96 | 3.71 | 2.1 | 2.6 | 3.0 | 3.8 | 8 (16) | 6 | 6 | 11 | 16 | 13 | 9 | 18 | 2 | 10 | 6 | 10 | |
| P | Marine | 3.21 | 3.61 | 4.17 | 6.04 | 3.3 | 3.7 | 4.3 | 6.1 | 11 | 8 | 9 | 11 | 14 | 13 | 12 | 26 | 9 | 7 | 6 | 8 | 1 |
| | Inland | 1.58 | 1.88 | 1.98 | 2.29 | 1.6 | 1.9 | 2.0 | 2.4 | 0 | 0 | 0 | 5 | 0 | 0 | 0 | 9 | 0 | 0 | 0 | 8 | |
| C | Marine | 3.43 | 4.67 | 6.08 | 10.01 | 3.5 | 4.7 | 6.2 | 10.1 | 6 | 7 | 8 | 12 | 10 | 10 | 11 | 17 | 6 | 4 | 3 | 3 | 3 |
| | Inland | 2.23 | 3.43 | 4.94 | 6.84 | 2.3 | 3.5 | 5.0 | 6.9 | 0 | 4 | 6 | 11 | 0 | 6 | 8 | 14 | 0 | 3 | 2 | 4 | |
| D | Marine | 3.38 | 4.45 | 6.18 | 10.15 | 3.4 | 4.5 | 6.2 | 10.2 | 10 | 8 | 8 | 12 | 18 | 16 | 11 | 28 | 10 | 7 | 4 | 5 | 3 |
| | Inland | 1.96 | 2.96 | 4.26 | 5.77 | 2.0 | 3.0 | 4.3 | 5.8 | 0 | 6 | 7 | 10 | 0 | 7 | 8 | 17 | 0 | 5 | 4 | 6 | |
| E | Marine | 3.43 | 4.70 | 5.94 | 9.74 | 3.5 | 4.8 | 6.0 | 9.8 | 8 | 7 | 5 | 12 | 14 | 12 | 6 | 24 | 8 | 5 | 2 | 5 | 3 |
| | Inland | 2.09 | 3.51 | 5.08 | 6.86 | 2.2 | 3.6 | 5.1 | 6.9 | 0 | 5 (10) | 7 | 12 | 0 | 8 | 9 | 16 | 0 | 5 | 4 | 5 | |
| F | Marine | 3.33 | 4.46 | 5.58 | 8.98 | 3.4 | 4.5 | 5.6 | 9.0 | 7 (10) | 9 | 6 | 12 | 10 | 18 | 8 | 22 | 6 | 8 | 3 | 5 | 3 |
| | Inland | 2.29 | 3.46 | 4.80 | 6.36 | 2.3 | 3.5 | 4.8 | 6.4 | 0 | 6 | 7 | 13 | 0 | 8 | 9 | 18 | 0 | 4 | 4 | 6 | |
| A | Marine | 5.02 | 9.56 | 11.22 | 20.28 | 5.1 | 9.6 | 11.3 | 20.4 | 13 | 20 | 18 | 34 | 20 | 26 | 50 | 67 | 8 | 5 | 9 | 7 | 6 |
| | Inland | 2.73 | 5.09 | 8.28 | 12.58 | 2.8 | 5.1 | 8.3 | 12.6 | 0 | 9 | 10 | 17 | 0 | 19 | 15 | 27 | 0 | 7 | 4 | 4 | |
| A (mill-scale) | Marine | 5.15 | 8.95 | 11.01 | 21.83 | 5.2 | 9.0 | 11.1 | 21.9 | 10 | 20 | 18 | 37 | 19 | 34 | 45 | 97 | 7 | 8 | 8 | 9 | 6 |
| | Inland | 2.98 | 5.42 | 8.27 | 12.33 | 3.0 | 5.5 | 8.3 | 12.4 | 5(2) | 8 | 7 | 17 | 6 | 13 | 9 | 27 | 4 | 5 | 2 | 4 | |

* Calculated from weight loss and specific gravity.

** Pit depths referred to the original surface of the metal either by measurement from an uncorroded surface or by calculation using the original and final average measured thickness of the same. Average of 20 deepest pits represents average of the 5 deepest pits measured on each side of duplicate specimens (area, 0.89 sq. ft.); values in parentheses indicate total number averaged when less than 20. Penetration of plate by deepest pit is indicated by "P".

*** Ratio of the deepest measured penetration to the average calculated penetration.

**** Visual inspection ranking based on observation of cleaned eight-year exposure panels. A total of eight surfaces were inspected (both sides of duplicate panels from the inland and marine exposures).

Figure 1—Duplicate mild steel panels exposed at Cristobal for eight years showing evidence of accelerated corrosion on bottom half of groundward side.

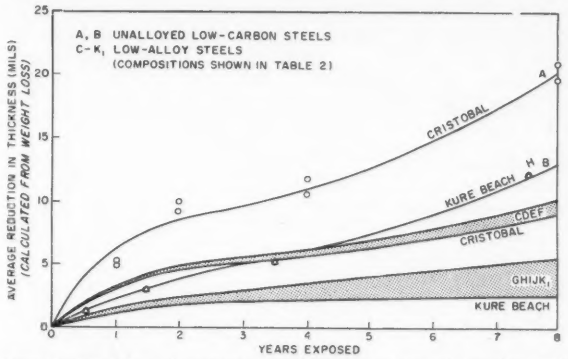


Figure 2—Comparison of corrosion of unalloyed low-carbon and low-alloy steels exposed to the marine atmosphere at Kure Beach, N. C., and at Cristobal, Canal Zone.

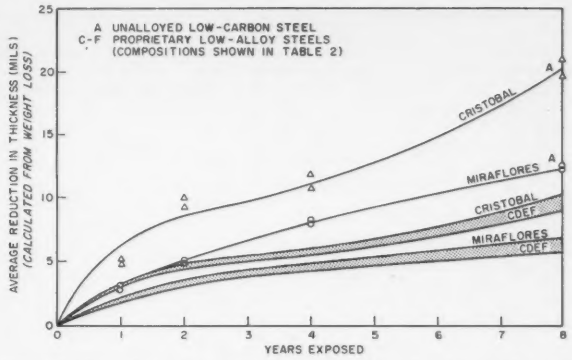


Figure 3—Comparison of atmospheric corrosion of unalloyed low-carbon and low-alloy steels at tropical marine and tropical inland sites in the Panama Canal Zone.

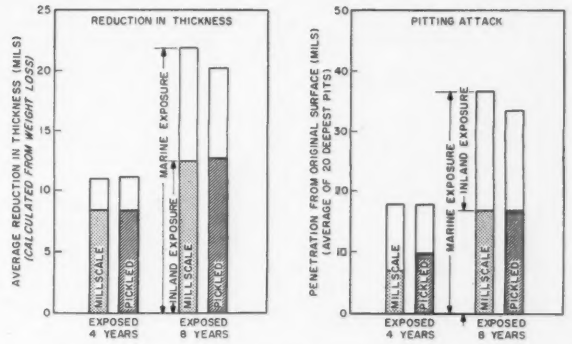


Figure 4—Comparison of millscale and pickled subsurfaces in corrosion resistance of unalloyed low-carbon steel exposed to tropical atmospheres.

was approximately 50 percent greater than for similar steels exposed at Kure Beach. Furthermore, unalloyed low-carbon steel corrodes approximately 50 percent faster at the tropical marine site than it does at the tropical inland site, while the unalloyed steel at the tropical inland site corrodes at approximately the same rate as similar steel at Kure Beach.

From the slope of the curves between four and eight years in Figure 2, it would seem that the corrosion rate begins to accelerate somewhat during this period. This was apparent for all of the steels in the Cristobal marine environment and for the unalloyed steel in the Kure Beach atmosphere; however, neither the low-alloy steels exposed at Kure Beach nor the steels exposed to the inland environment in the Canal Zone showed this tendency.

Larrabee[5] and Speller[6] have noted that the rate of atmospheric corrosion is dependent upon the length of time that moisture is in contact with the surface, the pollution in the atmosphere, and the composition of the steel. Since the composition of the steels is very similar, this increased corrosion rate in the tropics must be attributed to one or both of the remaining factors, (i.e., air pollution and/or increased contact with moisture.) Considering that the air pollution at both marine atmospheric sites is similar,[2,3] the increased rate of corrosion is in all probability due to the high yearly average humidity of 82 percent at the tropical site and the long periods of time during each day when the relative humidity is above 90 percent. Dearden[7] noted a marked increase in the rate of corrosion when the relative humidity is over 80 percent.

### Effect of Millscale

Although removal of millscale was part of the preparation for exposure of the test panels, so that all specimens would start the test with uniformly prepared surfaces, the question arose as to the actual effect of the millscale on the corrosion rate of the steel. It is sometimes conceded that where millscale is not removed some general protection is afforded by the scale, but with a probable acceleration of pitting in localized areas. In order to pursue this point, additional panels of the unalloyed low-carbon steel (steel A, Table 2) were exposed as received with the millscale attached. Figure 4 is a bar-graph showing the results following exposure for four and eight years, respectively. Average reduction in thickness, calculated from weight loss, and the pitting attack as the average measurement of the 20 deepest pits (5 from each side of duplicate panels) show that there was very little difference in either general or localized attack for either of the two surface conditions.

The pitting attack after eight years was slightly higher for the millscale panels in the marine atmosphere but the difference was much less than expected; at four years there was no measurable difference.

In the inland atmosphere the rate of pitting of the millscale and pickled panels was identical, and it is interesting to note that these values were approximately the same as the eight-year values for the marine exposure (i.e., 17 mils at the inland site after eight years and 18 mils at the marine location after four years.) Visual inspection of the eight-year panels indicated no significant effect of the millscale on the type and amount of corrosion.

### Effect of Low-Alloy Additions

*Copper-Bearing Steels*

A substanial increase in the corrosion resistance of mild carbon steel in temperate climates can be obtained by alloying with small amounts of copper in quantities of 0.1 percent to 0.5 percent. Larrabee[5] found that the presence of copper gave 35 percent reduction in corrosion for 7½ years in a marine environment at Kure Beach, N. C., and 40 percent reduction for the same period in an industrial atmosphere at Kearney, N. J. Hudson[8] reported 20 percent reduction in corrosion with the addition

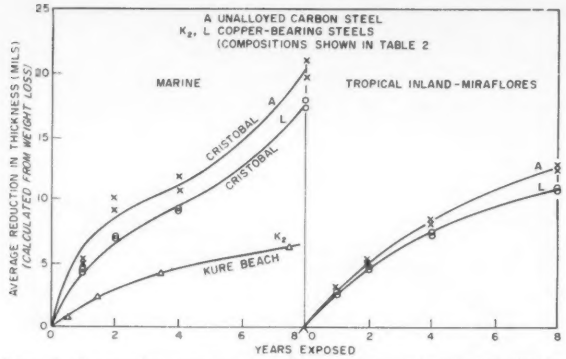


Figure 5—Comparative corrosion of unalloyed carbon steel and copper-bearing steel.

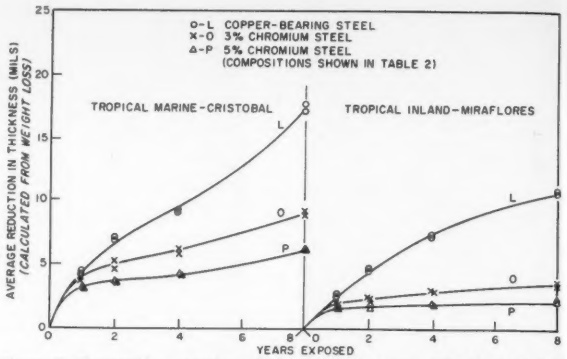


Figure 7—Comparative corrosion of chromium steel and copper-bearing steel exposed to tropical atmospheres in the Panama Canal Zone.

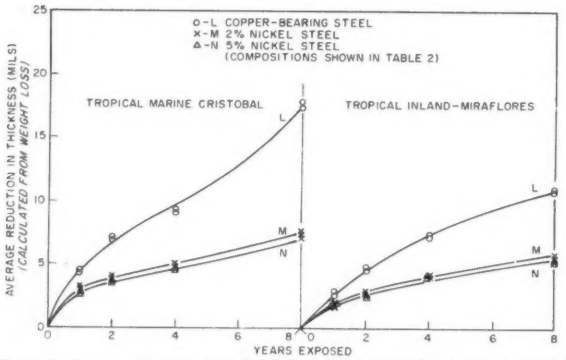


Figure 6—Comparative corrosion of nickel steel and copper-bearing steel exposed to tropical atmospheres in the Panama Canal Zone.

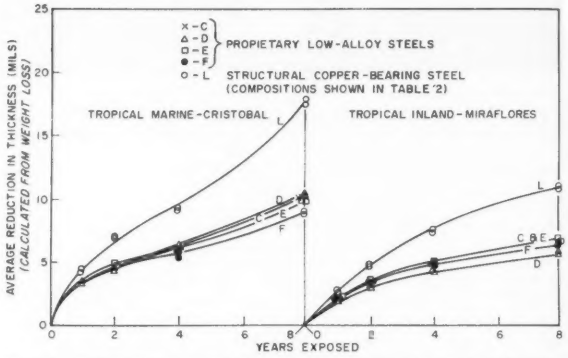


Figure 8—Comparative corrosion of four proprietary low-alloy steels and copper-bearing steel exposed to tropical atmospheres in the Panama Canal Zone.

of 0.5 percent copper during an eight-year exposure to a severe industrial atmosphere at Sheffield, England.

However, results from tests of copper-bearing and mild steel in a tropical marine environment at Key West, made by ASTM Committee A-5,[9] indicated that there was less advantage in using copper-bearing steel in the tropics. Evaluation of the data in Figure 5 indicates that in the present investigation also, copper-bearing steel (0.24 percent copper) had less advantage over mild carbon steel in these tropical atmospheres than would be found in other atmospheric environments. In the Canal Zone the improvement was only 13 percent for eight years in the Cristobal marine enviroment and 14 percent for eight years in the Miraflores inland atmosphere. In addition, Figure 5 shows that the eight-year corrosion of the coppear-bearing steel in the Canal Zone marine atmosphere was more than double that of a similar steel at Kure Beach, N. C.[3]

Visual inspection of the eight-year panels after cleaning revealed that the type and depth of corrosion attack were very similar on the copper and mild steels. Both metals were most heavily attacked in the center lower half of the underside of the panels exposed at a 30-degree angle (Figure 1).

Because of the small difference in cost, copper-bearing steel should be an obvious choice over unalloyed mild steel for any steel structure exposed to the atmosphere. In the subsequent evaluations of other low-alloy steels, copper-bearing steel rather than unalloyed steel will be used as criterion.

*Nickel Steels*

Hudson and Stanners[5] have reported that additions of nickel prove very beneficial for increasing resistance of steel to atmospheric corrosion. Larrabee[4] showed that a 54 percent reduction in the corrosion rate of mild steel may be obtained by including 2 percent nickel, and a 70 percent reduction with 5 percent nickel.

In the Canal Zone studies, two standard specification nickel steels were exposed in the tropical marine and inland atmospheres—i.e., a 2 percent nickel boiler steel conforming to RR Specification 3-A and SAE-2515 5 percent nickel steel (steels M and N, Table 2). As shown in Figure 6, each of the nickel additions was markedly beneficial in improving tropical atmospheric corrosion resistance, but surprisingly only very slight advantage was found for the 5 percent over the 2 percent nickel steel. In the Cristobal marine atmosphere the eight-year corrosion weight loss of the 2 percent nickel steel was 56 percent less than that of the copper-bearing steel, and the 5 percent nickel for the same condition was 59 percent less than the copper steel. At the Miraflores inland site the 2 percent and 5 percent nickel alloys were respectively 45 percent and 49 percent less corroded than the copper steel after an eight-year exposure.

Inspection of the cleaned eight-year exposure panels indicated that there was no discernible difference in depth of penetration and type of attack between the 2 percent and the 5 percent nickel steel plates. There were slightly deeper penetrations on the groundward side of the plates than on the skyward side, but the very heavy corrosion on the bottom, such as that shown in Figure 1, did not occur with the nickel alloy.

*Chromium Steels*

A 3 percent chromium steel and an AISI Type 501D 5 percent chromium steel were included in the Canal Zone corrosion investigation (steels O and P, Table 2). Chromium additions in these percentages are very effective for reducing the atmospheric corrosion of steel in temperate climates.[5, 8] In the tropical tests the two chromium alloys were markedly more resistant to corrosion than the copper-bearing steel as shown in Figure 7. With respect to weight loss, the reduction was 47 percent for the 3 percent chome steel and 64 percent for the 5 percent chrome steel in comparison with the copper steel after exposure for eight years at the Cristobal marine site. Even better results were obtained at the Miraflores inland site, where the 3 percent and 5 percent chromium steels showed improvements of 66 percent and 80 percent, respectively.

Unlike the nickel steels where 5 percent nickel showed only a slight advantage over the 2 percent nickel, the 5 percent chromium steel was appreciably more corrosion resistant than 3

percent chromium. This effect was especially noticeable with the eight-year Cristobal panels after removal of the corrosion product. These cleaned specimens revealed that the 5 percent chromium steel had corroded very uniformly with practically no pitting, and the corroded surface was the smoothest of any of the steels. The general surface of the 3 percent chromium panels was smoothly corroded, but the bottom half of the groundward side closely resembled the copper-bearing steel, with the characteristic accelerated pitting in this area, such as that shown in Figure 1.

*Proprietary Low-Alloy Steels*

Low-alloy steels containing small amounts of various alloying elements, compounded and trademarked by different manufacturers, have been recognized for many years as having excellent resistance to atmospheric corrosion in temperate zones. The present investigation included four well-known brands of these proprietary low-alloy steels (steels C-F, Table 2). Figure 8 presents the eight-year corrosion curves of these four metals in tropical marine and tropical inland exposures with comparative curves for copper-bearing steel. The corrosion weight loss in the Cristobal marine atmosphere was from 40 percent to 50 percent less for the four low-alloy steels than for the copper steel panels. At the Miraflores inland location a 35 percent to 50 percent reduction over the copper steel was obtained. Larrabee[3] investigated the corrosion of a group of five similar low-alloy steels at Kure Beach and found 24 percent to 59 percent improvement over a copper steel during 7½ years of exposure.

One of the significant aspects of the group of curves in Figure 8 is the remarkable similarity in the corrosion rates of the four differently compounded low-alloy steels. The band is so narrow that no definite ranking can be established. On the basis of small differences, steel F gave the best results in the marine exposure, and Steel D, the best in the inland atmosphere. Steel D, incidentally, was by a slight margin the least resistant of the four in the marine environment.

The cleaned eight-year low-alloy panels revealed that the corrosion was not as uniform over the general surface as it was in the nickel and chromium steel samples. Steel E, the one steel containing molybdenum, possessed a visibly rougher corrosion pattern than the other three low-alloy steels; however, in all of the low-alloy steels, the accelerated pitting on the groundward side shown in Figure 1 was significantly reduced.

## Conclusions

1. The corrosion of structural steels for an eight-year exposure was from 1.5 to 2.2 times higher in the tropical marine atmosphere of the Canal Zone than in a temperate marine atmosphere.

2. The effects of the tropical marine and tropical inland exposures in Panama have been compared and it was determined that the marine atmosphere resulted in 1.7 times more corrosion weight loss after an eight-year exposure of mild steel.

3. No difference in type or extent of corrosion was evident between pickled and millscale surfaces on mild carbon steel in either of the tropical atmospheres.

4. Copper-bearing steel was less effective in retarding corrosion in the tropical atmospheres than in temperate zones. The corrosion of copper steel in the two tropical atmospheres was only 13 percent and 14 percent less than that of the unalloyed mildsteel.

5. The 2 percent and 5 percent steels were very effective in resisting corrosion. After the eight-year exposure the nickel steels were corroded 45 percent to 59 percent less than the copper-bearing steel. The RR Specification 3-A, 2 percent nickel inhibited corrosion almost as effectively as the SAE-2515 5 percent nickel steel.

6. The corrosion resistance of chromium steel was comparable to that of nickel steel. The AISI Type 501D 5 percent chromium steel proved slightly superior to both nickel steels in the marine exposure and appreciably better at the inland location. The 3 percent chromium steel gave slightly better results than the nickel steels in the inland atmosphere but poorer results at the marine location.

7. The four proprietary low-alloy steels displayed good resistance to tropical atmospheric corrosion; the weight loss for eight years was 36 percent to 49 percent less than that of the copper-bearing steel. The difference in corrosion resistance of the four differently compounded low-alloy steels was insignificant.

## Acknowledgments

Special acknowledgment is made of the contributions of H. W. Mundt who helped plan much of the experimental work and who, until his death in 1953, was Scientist-in-Charge of the Canal Zone Corrosion Laboratory. Also, the contributions of L. J. Thompson are gratefully acknowledged. The support of The Panama Canal Company and the Engineer Research and Development Laboratories, Fort Belvoir, has been indispensable in the course of this work. The interest of E. M. Browder and George Howard of these organizations respectively has been particularly helpful.

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**Any discussions of this article not published above will appear in the December, 1958 issue**

# A Method For Determining Corrosion Rates From Linear Polarization Data*

By MILTON STERN*


## Abstract

A method for determining corrosion rate from electrochemical polarization data obtained in the region of the corrosion potential is described. The technique has foundation in theory, is supported by experimental evidence, and appears to have widespread application. The advantages and limitations of the method are discussed.

It would appear that the use of linear polarization measurements can supply valuable information regarding: (1.) Studies of the effect of environment variables on corrosion rate. These include changes in composition, velocity, and temperature, (2.) Evaluations of inhibitors in controlling corrosion, (3.) Comparison of the corrosion rates of various alloys of similar composition in a given environment, and (4.) Determination of changes in corrosion rate with time, including studies of underground structures as well as materials in aqueous solutions.

It also may be possible to use this method in evaluating the condition of coatings in service which cannot be inspected by visual methods. 2.3.5


## Introduction

CORROSION TESTING by weight-loss methods is generally a long, tedious affair which often does not produce completely satisfactory results. This is particularly true when the corrosion rate changes with time.

Several attempts to relate various electrochemical properties of a metal to corrosion rate have been described in the literature. Unfortunately, the techniques usually are more involved than weight-loss procedures and furthermore they may have no sound basis in theory. Recently, however, Skold and Larson[1] and Simmons[2] have described empirical observations which appear to have promise as a practical method for measuring instantaneous corrosion rates by electrochemical means. They showed that the slope of the linear portion of the polarization curve of iron can be related to its corrosion rate. The method has some foundation in theory and may have rather wide applicability to many systems.

The purpose of this discussion is (a) to describe the theoretical basis which makes the method attractive, (b) to define the conditions where the technique appears to be most applicable, and (c) to provide supporting evidence.

## Description of the Method

It is often found experimentally that the initial portion of a polarization curve is linear so that potential plotted as a function of applied current or current density approximates a straight line. The slope of this straight line, $\Delta E/\Delta I$, has units of resistance and for convenience will be called the "polarization resistance." It is important to note that this is not a resistance in the usual sense. The nature of "polarization resistance" will be discussed in a later section.

Simmons,[2] in a study of polar organic inhibitors in crude oil-salt water systems, found that a qualitative relation existed between $\Delta E/\Delta I$ and the corrosion rate. He reported that all inhibitors which exhibit good weight-loss suppression give high values of "polarization resistance." The converse was also true. In addition, simultaneous measurement of $\Delta E/\Delta I$ and weight change as a function of time showed that "polarization resistance" increases as inhibition proceeds reaching a maximum when the sample apparently stops corroding.

Skold and Larson[1] initially conducted polarization measurements to calculate corrosion rates from "breaks" in polarization curves by a method described by Schwerdtfeger and McDorman.[3] This approach was abandoned for reasons described in their paper. They found in their studies of steel and cast iron in natural waters that a linear relation existed between potential and applied cathodic and anodic current density at low values of applied current density. "Polarization resistance" was higher for samples having a low corrosion rate than for samples exhibiting high rates. Fortunately, their conditions were such as to give corrosion rates which varied over several orders of magnitude. A plot of corrosion rate versus "polarization resistance" on logarithmic scales gave a straight line with a negative slope. This empirical data was used to determine changes in corrosion rate with time for various systems.

## Theoretical Basis for the Method

Stern and Geary,[4] in a discussion of the shape of polarization curves for corroding systems controlled by activation polarization,(1) showed that a linear relationship is expected in the region where the polarized potential is close to the corrosion potential. For these conditions, the following equation was derived.

$$\frac{\Delta E}{\Delta I} = \frac{\beta_a \beta_c}{(2.3)(I_{corr})(\beta_a + \beta_c)} \qquad (1)$$

where $\Delta E/\Delta I$ is the polarization resistance, the constants $\beta_c$ and $\beta_a$ are the slopes of the logarithmic local cathodic and anodic polarization curves, and $I_{corr}$ is the corrosion current. This equation applies only when $\Delta E$ is small.(2) Thus, it is seen that the "polarization resistance" is inversely proportional to the corrosion current. Equation (1), however, does not consider the influence of concentration polarization which undoubtedly played an important role in the systems of Simmons[2] and Skold and Larson[1]. Thus, it is necessary to determine whether the polarization curve for corroding systems controlled by concentration polarization exhibits a linear section and whether the slope of this linear section is related to corrosion rate. To accomplish this, it is first convenient to consider concentration polarization on a non-corroding electrode and then introduce the additional complexity arising when the electrode corrodes.

Concentration polarization occurs at a cathode when the reaction rate or the applied cathodic current is so large that the substance being reduced cannot reach the cathode at a sufficiently rapid rate. The solution adjacent to the electrode surface becomes depleted of the reacting ions, and the rate then is controlled by the maximum rate at which the reacting species can diffuse to the surface. The electrode potential changes sharply in this region until a potential is reached where a new reaction proceeds. The change in potential caused by concentration polarization can be expressed in its most simple form as[5]

$$E_{conc} = 2.3 \frac{RT}{nF} \log \left(1 - \frac{I}{I_L}\right) \qquad (2)$$

where $I_L$ is the limiting diffusion current or the current equivalent to the maximum rate of diffusion of the reacting substance. By assigning arbitrary values to the constants ($2.3\frac{RT}{nF} = 0.059$ volt, and $I_L = 100$ microamperes), the shape of the curve described by Equation 2 may be illustrated in Figure 1.

The series expansion of $\ln(1+X) = X - \frac{1}{2}X^2 + \frac{1}{3}X^3 - \frac{1}{4}X^4 + \ldots$ can be used to estimate how concentration polarization varies with current for small values of $\frac{I}{I_L}$. For this condition, only the first term of the series is significant so that at 25 C

$$E_{conc} = -\frac{RT}{nF}\frac{I}{I_L} = -0.0256\frac{I}{I_L} \qquad (3)$$

Thus, when the applied current is small in comparison to the limiting diffusion current, concentration polarization approximates a linear function of current with a slope of $0.0256/I_L$. The plot of Equation 3 has been drawn on Figure 1 to illustrate the extent of its applicability.

When one considers a corroding electrode whose corrosion rate is controlled by concentration polarization, the situation is slightly different. The schematic

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* Metals Research Laboratories, Electro Metallurgical Company, Division of Union Carbide Corporation, Niagara Falls, New York.

(1) For systems where the local anodic and cathodic polarization curves are logarithmic in nature.

(2) The expected range of the linear relation between E and I and the deviation from linearity for various potential values are described in the appendix.

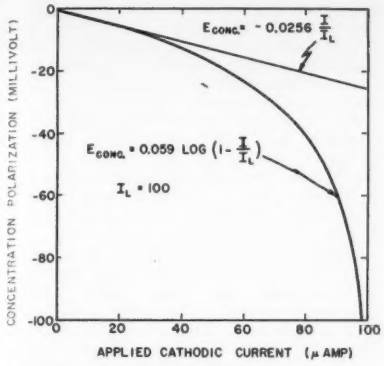
$E_{CONC.} = -0.0256 \frac{T}{I_L}$
$E_{CONC.} = 0.059 \log\left(1 - \frac{I}{I_L}\right)$
$I_L = 100$
CONCENTRATION POLARIZATION (MILLIVOLT)
APPLIED CATHODIC CURRENT (μ AMP)

Figure 1—A concentration polarization curve showing the extent of the linear region.

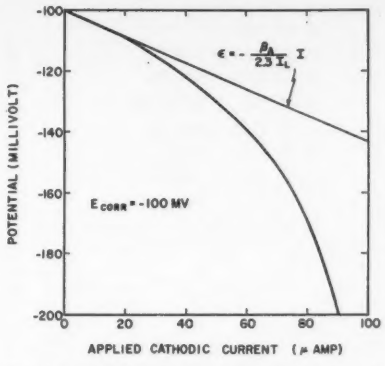


Figure 3—Potential as a function of applied current for the system described in Figure 2.

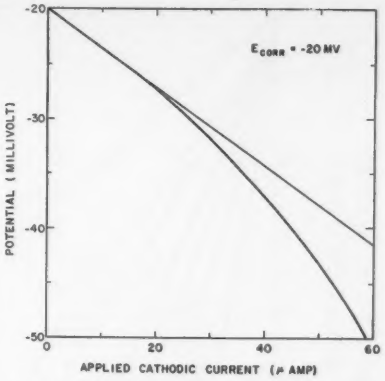


Figure 4—Potential as a function of applied current for a corroding system similar to that shown in Figure 2 except that the anodic curve is moved upward to produce a corrosion potential of 0.02 volt.

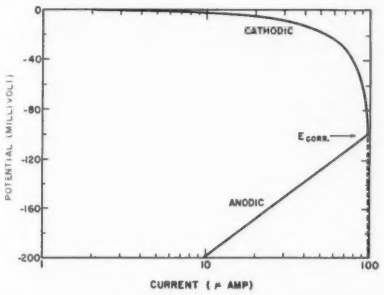


Figure 2—Polarization diagram for a corroding metal with a logarithmic anodic polarization curve and a cathodic polarization curve exhibiting concentration polarization.

polarization diagram for such a condition is illustrated in Figure 2 where the anodic polarization curve is considered logarithmic in nature. For such a system, the corrosion current is practically equal to the limiting diffusion current. It is well known[6] that the applied cathodic current necessary to polarize such a corroding electrode to some given cathodic value is given by the following relationship:

$$I_{applied} = I_c - I_a \qquad (4)$$

where $I_c$ and $I_a$ are the local cathodic and anodic currents, respectively. Also, the equation for the change in anodic current, using the corrosion potential as reference, may be written

$$I_a = I_{corr}\left(10^{\frac{\varepsilon}{\beta_a}}\right) \qquad (5)$$

where $\varepsilon$ is the difference between the polarized potential and the corrosion potential. Since $I_c = I_{corr} = I_L$, substitution of Equation (5) into Equation (4) produces

$$I_{applied} = I_L - I_L\left(10^{\frac{\varepsilon}{\beta_a}}\right) \qquad (6)$$

For small values of $\varepsilon$, that is where the polarized potential is close to the corrosion potential, expansion of the exponential and rearrangement yield

$$\varepsilon = -\frac{\beta_a}{2.3\, I_L} I_{applied} \qquad (7)$$

or

$$\frac{\Delta E}{\Delta I} = -\frac{\beta_a}{2.3\, I_L} = -\frac{\beta_a}{2.3\, I_{corr}} \qquad (8)$$

Therefore, a corroding electrode controlled by concentration polarization also produces a linear polarization curve, the slope of which is related to the corrosion current.[3] Figure 3 shows the cathodic polarization curve of the system illustrated in Figure 2 calculated from Equations (4) and (5). The arbitrary constants for the calculation are $I_L = 100$ microamperes, $\beta_a = 0.1$ volt, and $E_{corr} = -0.1$ volt.

Equation (8) applies only when the anodic polarization curve intersects the cathodic curve close to the limiting diffusion current so that $I_c$ may be considered a constant. If this is not true, such an equation cannot be simply derived. This does not mean necessarily that under such circumstances quasi-linear behavior will not be observed, but the inverse relation between "polarization resistance" and corrosion current described by Equation (8) does not apply.

For example, consider a system with the same cathodic polarization curve illustrated in Figure 2 and an anodic curve of similar slope intersecting at 0.02 volt where $I_c$ is not a constant. This is equivalent to moving the anodic curve of Figure 2 upward. Figure 4, which shows the cathodic polarization curve for such a system calculated in the manner described previously, reveals that quasi-linear behavior does exist. Furthermore, the slope of this portion of the polarization curve is greater than that shown in Figure 3 where the corrosion rate is greater. Thus, qualitatively, $\frac{\Delta E}{\Delta I}$ increases as $I_{corrosion}$ decreases. This is important since it is believed that the real value of this approach at the present time lies not in direct calculation of corrosion rates from equations such as (1) and (8), but rather in an empirical determination such as used by Skold and Larson.[1]

There are several reasons for adopting this attitude. First, the constants required to apply Equation (1) or (8) are not available for many real systems. Secondly, the constants may not remain constant as environmental conditions change. Also, it is possible that the local anodic polarization curve is not logarithmic in nature since concentration polarization may play a role in anodic polarization, or the anodic curve may actually be linear as described by Petrocelli[7] for dissolution of aluminum in alkaline solutions. In addition, an IR drop may be included in the polarization measurements. This would not distort the linear shape of the pertinent portions of the polarization curve but would, of course, increase the value of $\frac{\Delta E}{\Delta I}$. This resistance error, which was recognized by Skold and Larson,[1] is evident in their empirical relationship between $\frac{\Delta E}{\Delta I}$ and corrosion rate. If the corrosion rate is inversely proportional to "polarization resistance" as indicated by Equations (1) and (8), then a plot of these two parameters on logarithmic scales should give a straight line with a slope minus one. The slope of the line drawn by Skold and Larson[1] is greater than this for data obtained in 3000 ohm-cm water. Their data in low resistance solutions lie close to the theoretical slope.

Perhaps the most important reason for considering that an empirical determination of the quantitative relation between "polarization resistance" and corrosion rate is necessary, lies in the fact that determination of $\frac{\Delta E}{\Delta I}$ depends heavily on the judgment which an investigator uses to determine the extent of the linear polarization curve. An insufficient number of experimental points and scatter in the data of a few millivolts often will tend to extend the apparent linear portion of a polarization curve to higher potentials resulting in inaccurate values of polarization resistance.[4] As described in the appendix, truly linear dependence of potential on applied current is expected only for about the first 10 millivolts of polarization.

## Experimental Observations

Equation (1) applies to any system whose potential is determined by two

(3) Equation (8) can be derived directly from Equation (1) since the conditions selected are equivalent to considering $\beta_c$ infinite. Thus,

$$\lim_{\beta_c \to \infty} \frac{\beta_a \beta_c}{(2.3)\,(I_{corr})\,(\beta_a + \beta_c)} = \frac{\beta_a}{(2.3) I_{corr}}.$$

(4) When concentration polarization is involved, the measured "polarization resistance" will tend to be too high, whereas if only activation polarization occurs, the measured "polarization resistance" will be low. This occurs because of the different shapes of concentration polarization and activation polarization when plotted on a linear scale.

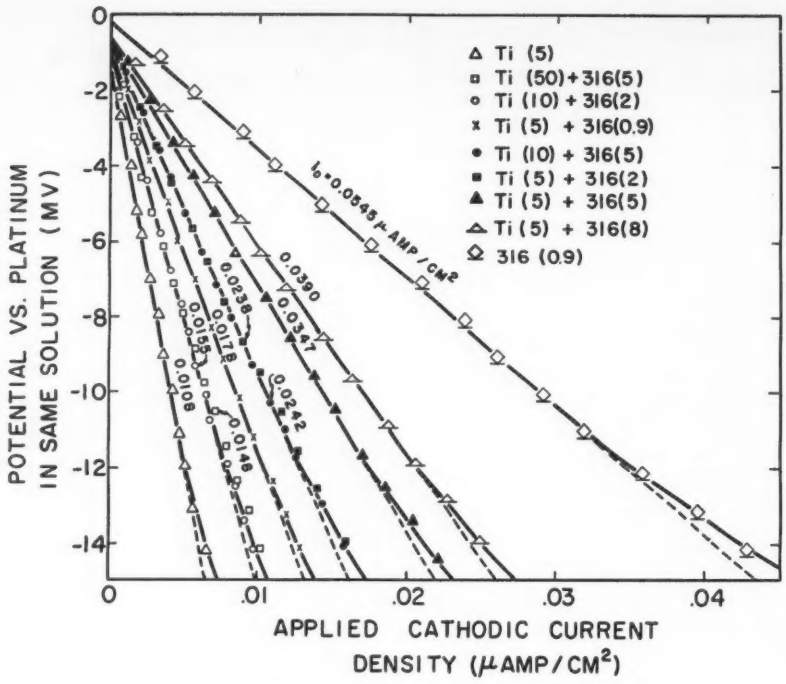


Figure 5—Potential as a function of applied cathodic current density for various bi-electrodes.

intersecting logarithmic polarization curves. Therefore, in addition to corroding electrodes, reversible electrodes also can be described by this equation simply by substituting exchange current for corrosion current.

A reversible electrode system was selected for experimental verification primarily because an obvious, well behaved system was readily available.

Some earlier work[8] showed that titanium and Type 316 stainless steel in nitrate containing solutions of ferrous and ferric chloride exhibit potentials very close to the reversible ferric-ferrous potential of the solution. In addition, it was found that the exchange current density for the reaction $Fe^{++} + e \rightleftarrows Fe^{+++}$ was markedly different when it occurs on the surface of the two metals. Also, it was shown[9] that the exchange current density on bi-electrodes (couples) made of these two materials could be represented by the following equation.

$$i_{o(Ti+316)} = f_{316}\, i_{o(316)} + f_{Ti}\, i_{o(Ti)}$$

where $f_{316}$ and $f_{Ti}$ represent the fraction of the couple area occupied by Type 316 stainless steel and titanium, respectively; $i_{o(316)}$ and $i_{o(Ti)}$ are the exchange current densities for the individual materials; and $i_{o(316+Ti)}$ is the exchange current density of the bi-electrode. Bi-electrodes are formed by electrically coupling different areas of the two metals. Thus, the use of bi-electrodes with various area fractions of titanium and Type 316 stainless provides an ideal system for obtaining surfaces with a range of exchange current densities which vary from the low value on titanium itself to the high value on stainless steel. This permits an experimental check of the inverse relationship between "polarization resistance" and exchange current as predicted by Equation (1).[5]

The samples, procedures, and equipment were exactly the same as those described previously[9] except that in this case, it was necessary to get many accurate points on a polarization curve in the potential region from 0 to 15 millivolts. This was accomplished, without reducing the impedance of the potential measuring system, by using an Applied Physics Corporation Model 31 vibrating reed electrometer as a null point indicator in series with a precision potentiometer. The electrometer has a four-inch 0- to 1-millivolt scale which permits potential measurement to better than 0.01 millivolt. Six samples, contained in the same polarization cell, were used to produce the bi-electrodes. They are designated at Ti(5), Ti(10), Ti(50), 316(0.9), 316(2), and 316(5) where the prefix indicates the material, and the number in parentheses approximates the surface area in square centimeters. Inasmuch as exact areas along with the measured exchange current densities have been published previously[9] this information will not be repeated here.

Figure 5 shows the low potential cathodic polarization region for various bi-electrodes which were selected to give a range of exchange current densities between the values which apply to titanium and 316 stainless steel. The exchange current densities, calculated from the preceding equation are included on the figure.[6] In those cases where the bi-electrode exchange current density was actually determined,[9] the agreement between measured and calculated values was good. Figure 6 illustrates the inverse relation between "polarization resistance" and exchange current density as predicted by Equation (1). When these data are plotted in this manner, it is important to note that "polarization resistance" should be zero when the exchange current density is infinite.

Additional support for this kind of analysis can be obtained from the data of Bonhoeffer and Jena[10] who studied the electrochemical behavior of 11 different types of iron in sulfuric acid solutions. These authors compared "polarization resistance" and corrosion current for these materials and showed that the corrosion rate decreases as "polarization resistance" increases. Their plot of "polarization resistance" versus corrosion current appears to be hyperbolic in nature. Figure 7 illustrates their data plotted in the same manner as Figure 6 and shows the inverse relation between "polarization resistance" and corrosion current. Since it is most likely that activation polarization controls corrosion rate under the conditions of their test, Figure 7 supplies additional confirmation of Equation (1) and indicates that such electrochemical measurements can supply a valuable screening method.

### General Features of the Method

"Polarization resistance," as used here, is not a resistance in the usual sense of the term. The linear dependence of potential on current only exists because the difference between two logarithmic functions of current (Equation (4)) approximates a linear function when the logarithmic functions are of the same order of magnitude.

"Polarization resistance" measured by either anodic or cathodic polarization should be identical. This not only results from the derivation of Equations (1) and (8) but also is observed experimentally.[5] Skold[11] has confirmed this, but reports that the extent of the linear relation observed during anodic polarization is smaller than that observed during cathodic measurements.

The extent of the linear relation described by Equation (1) is dependent upon the beta values of the individual anodic and cathodic polarization curves. It is possible to analyze Equation (1) mathematically to show the amount of polarization which can occur for systems with various beta values while maintaining a linear relation within various error limits. To do this, it is necessary to assume that the anodic and cathodic beta values are equal. While this is not necessarily the case for many real systems, it provides a valuable guide in interpretation of experimental data. Such an analysis is presented in the appendix and shows that the maximum error in potential (designated by e) can be described by Equation (9).

$$e = \frac{\beta I^3}{48 \ln 10\ I^3_{corr}} \qquad (9)$$

In the region where current approximates a linear function of potential, the value e is the maximum deviation of potential from linearity at any current. For a reversible electrode, the corrosion current in Equation (9) would be replaced

[5] Actually, one may compare either "polarization resistance" to exchange and corrosion current or "polarization resistance per unit area" to exchange or corrosion current density. The use of corrosion current density only serves to compare samples of different size under the same conditions and has no direct relation. In this case, to the actual anodic or cathodic current densities which exist during corrosion.

[6] The Ti(10) electrode exhibited a lower exchange current density than the other titanium samples. This is not considered serious for present purposes, since actual experimental values for each electrode have been used to calculate the exchange current current of bi-electrodes.

[7] One point which appeared abnormal has not been included.

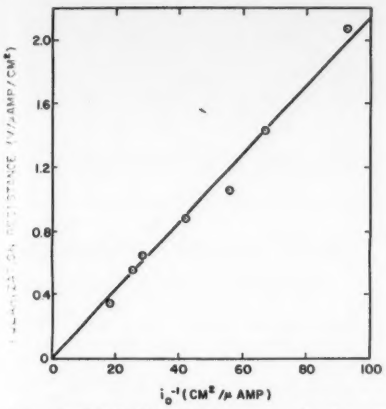


Figure 6—Polarization resistance as a function of the reciprocal of the exchange current density for various bi-electrodes.

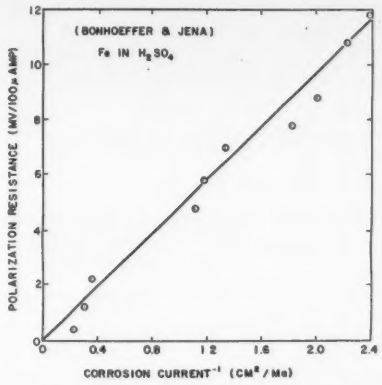


Figure 7—Polarization resistance as a function of the reciprocal of corrosion current for various iron samples in sulfuric acid (Bonhoeffer and Jena).

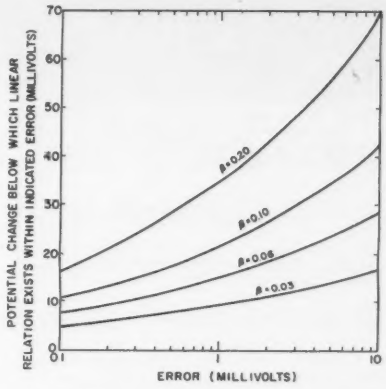


Figure 8—The amount an electrode may be polarized and still exhibit linear polarization behavior as a function of the deviation from linearity for various beta values.

by the exchange current. Using Equation (9) and the known relation between potential and applied current in the linear region (see appendix), it is possible to calculate the value of polarized potential below which a linear relation is expected within any given error. This is shown in Figure 8 for a variety of beta values and reveals that a system with anodic and cathodic beta values of 0.1 can be polarized for about 10 millivolts with a maximum deviation from linearity of 0.1 millivolt, or it may be polarized 21 millivolts with a maximum deviation from linearity of 1.0 millivolt.

The use of the "polarization resistance" for measuring corrosion rates has one particularly important advantage. The potential range investigated is close to the corrosion potential and the applied currents are generally smaller than the corrosion current. Thus, the nature of the surface is not changed significantly, and the reactions which proceed during polarization are those which actually occur during the corrosion process. This is not necessarily the case when a corroding surface is markedly polarized, since under such conditions, the subsequent corrosion rate may be affected for some time after polarization has been discontinued.

The following is a list of situations where it appears that the use of linear polarization measurements can supply valuable information.

1. Studies of the effect of environment variables on corrosion rate. These include changes in composition, velocity, and temperatures.

2. Evaluation of inhibitors in controlling corrosion.

3. Comparison of the corrosion rates of various alloys of similar composition in a given environment.

4. Determination of changes in corrosion rate with time, including studies of underground structures as well as materials in aqueous solutions.

5. It also may be possible to evaluate the condition of coatings in service which cannot be inspected by visual methods.

While the use of linear polarization data to determine corrosion rates cannot be considered a universal approach, there is sufficient basis in theory along with supporting evidence to believe that the technique can find a useful place in corrosion studies.

### Acknowledgment

The author would like to acknowledge the skillful assistance of E. A. Tomes who conducted the experimental measurements, and E. J. Bartolomei and N. Darroch who carried out many of the calculations. Dr. L. Cross assisted in the derivation of Equation (17).

## APPENDIX

Since the use of polarization data to determine corrosion rates requires a measurement of the slope of the linear region of a polarization curve, it is necessary to know the approximate extent of the linear region. This is best described by indicating the potential change during polarization below which the polarization curve is linear within a given potential error. Consider a corroding system whose potential and corrosion rate are determined by two intersecting logarithmic polarization curves with equal beta values. When the metal is polarized by an external applied cathodic current, the following relation applies:

$$I_{applied} = I_c - I_a \qquad (10)$$

Since $I_c$ and $I_a$ are equal at the corrosion potential and are logarithmic functions of potential

$$I_{applied} = I_{corr}\left(10^{-\frac{\varepsilon}{\beta}} - 10^{+\frac{\varepsilon}{\beta}}\right) \qquad (11)$$

where $\varepsilon$ is the difference between the polarized potential and the corrosion potential.

Rearranging gives

$$I_{applied} = -I_{corr}\left(e^{+\frac{\varepsilon}{\beta}\ln 10} - e^{-\frac{\varepsilon}{\beta}\ln 10}\right) \qquad (12)$$

and

$$I_{applied} = -2\, I_{corr} \sinh\frac{\varepsilon}{\beta} \ln 10 \qquad (13)$$

Therefore,

$$\varepsilon = \frac{\beta}{\ln 10} \sinh^{-1}\left(\frac{I_{applied}}{2\, I_{corr}}\right) \qquad (14)$$

Using the series $\sinh^{-1} X = X - \frac{1 \cdot X^3}{2 \cdot 3} + \frac{1 \cdot 3 X^5}{2 \cdot 4 \cdot 5} - \frac{1 \cdot 3 \cdot 5 X^7}{2 \cdot 4 \cdot 6 \cdot 7} + \ldots,$

$$\varepsilon = -\frac{\beta}{2 \ln 10}\frac{I_{applied}}{I_{corr}} + \frac{\beta}{48 \ln 10}\frac{I^3_{applied}}{I^3_{corr}} - \ldots \qquad (15)$$

The first term on the right side of Equation (15) shows the inverse relation between $\frac{\Delta E}{\Delta I_{applied}}$ and $I_{corr}$[8]. Thus, the subsequent terms are the error (designated by e) in $\varepsilon$ if only the first term is considered. Therefore,

$$e = \frac{\beta}{48 \ln 10}\frac{I^3_{applied}}{I^3_{corr}} - \ldots \qquad (16)$$

However, since the right side of Equation (15) is an alternating series, it can be shown that the error in using the first term of the series is bounded by the first neglected term.

Hence

$$e \leqslant \frac{\beta}{48 \ln 10}\frac{I^3_{applied}}{I^3_{corrosion}} \qquad (17)$$

Thus, for given values of e and $\beta$, one may calculate the ratio of applied current to corrosion current and use this in Equation (11) or (14) to calculate $\varepsilon$ which is the amount an electrode has been polarized. This value of potential shows how far one may polarize a surface and expect linear behavior within the error selected. This is the basis of Figure 8.

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[8] Actually, Equation (1) applies to a system with different beta values, whereas this analysis considers the anodic and cathodic beta values equal (see Reference 4) in order to simplify the mathematics. While it is recognized that this is not the case for many real systems, the determination of the extent of the linear relation for such conditions provides a valuable guide in interpretation of experimental data.

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**Any discussions of this article not published above will appear in the December, 1958 issue**

## *TECHNICAL PAPERS ON CORROSION WELCOMED*

**Authors of technical papers on corrosion are invited to submit them for review without invitation to the Editor of Corrosion. Write for "Guide for the Preparation and Presentation of Papers" sent free on request to prospective authors.**

444t

# Water Industry Corrosion Problems Discussed

## Increasing Damage From Deicing Salts Is Feared

A study of residual deicing salt in manholes and apprehension that salting will increase underground corrosion were principal topics considered at the meeting of Unit Committee T-4D on Corrosion by Deicing Salts.

A report was made on the joint study being made by the Niagara-Mohawk Power Co. and the New York Telephone Co. of the salt content of 25 manholes in Buffalo. In some of the manholes where the salt content reached a high level during the winter it remained at a high but somewhat lower level during the summer. In other manholes the salt content dropped by a very large factor during the summer. The report later was printed and attached to minutes of the meeting.

### Correlation Not Good

One corrosion engineer said he had obtained a correlation between weight loss and the salt content of manholes. Another person pointed out that in Chicago the decrease in street railways and salting at track switches has led to a decrease in the corrosion rate in such areas, but the total number of failures including both cathodic and anodic conditions has not changed significantly. It was said that in the New York area, anodic underground corrosion was increasing as salting increased. One observer said that in the Detroit area, since the removal of the street railway system, the corrosion rate on the Detroit Edison underground cable system has increased. Most of this has occurred on a 4.8 kv system and is due to differential aeration.

General apprehension was expressed that the increasing amount of salting is raising underground conductivity to such an extent that corrosion cells of all kinds are being activated to an abnormal degree. It was reported that the last streetcar line in Milwaukee was discontinued in February 1958. Accompanying the elimination of trolleys from the streets has been a rise in corrosion, the rate in 1957 being two times the average for the last nine years.

### Aircraft Damage Noted

Deicing salts on airport runways have an obvious effect on aircraft and ground equipment it was said. Tests made by Air Force personnel on various salt combinations with and without inhibitors developed none which were sufficiently low in corrosivity.

A paper on Cathodic Protection of Lead Cable Sheath in the Presence of Alkali from Deicing Salts by W. H. Bruckner and W. W. Lichtenberger, presented at the 14th Annual NACE Conference was discussed. Also considered was a request from NACE for a list of corrosion problems for research to be sent to Aaron Wachter, chairman of the NACE Research Committee.

## *Static Inhibitor Test Completion Urged by T-1K*

Quick formulation and approval of static inhibitor screening tests was recommended to T-1K Inhibitors for Oil and Gas Wells at a March 19 meeting in San Francisco. This recommendation was made so the committeemen could turn their attention to evaluation testing procedures, for which there was reported to be a pressing need.

The committee heard a report on questionnaire circulated by T-1K-1 Sour Crude Inhibitor Evaluation in which recommendations are made for a Standard Static Test. Subcommittee approval is being solicited.

The group heard also a discussion of dynamic testing procedures in which it was concluded a technically sound dynamic tests to screen sweet crude corrosion inhibitors was feasible. Some of the relationships between oil and water in these tests were mentioned.

## Sea Water Silt Tests Are Planned for Anodes

Tests of cathodic protection anodes in sea water silt will be made and reports on current drains made to NACE Technical Unit Committee T-2B Anodes for Impressed Current. This was one of the developments at the March 20 meeting of the committee at San Francisco.

Other information presented included a report showing substantially less loss in weight of high silicon anodes vs graphite anodes installed in both fresh and sea water in the Northeast. It was recommended that tables in a third interim report on the use of high silicon anodes show hole diameters when they are backfilled with coke breeze.

A discussion concerning "necking" of graphite anodes in sea water included a report on placing the anodes in a pattern like spokes of a wheel, with lead wires in the center. A concrete ring then was cast around tops of the anodes and the enclosed space filled with coal tar. This stopped necking. It was suggested also that fully treated Type NA anodes would not neck under the conditions discussed.

Organization of a group to collect data on deep anode installations was recommended.

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The Ten-Year Index to CORROSION 1945-54 indexes over 3500 pages published in those years.

## *Poor Materials Selection, Bad Design Called Main Troubles*

The demand for high performance at low cost for materials used in the water utility industry; poor communications between manufacturers and engineers and lack of follow through to check decoatings will be released for publication points discussed at a technical committee meeting held March 17, 1958. A meeting of T-4F on Materials Selection for Corrosion Mitigation in the Utility Industry and of T-4F-1 on Materials Selection in the Water Industry was held during the 15th Annual NACE Conference.

F. E. Kulman, Consolidated Edison Company of New York, chairman of T-4F, explained that the T-4F-1, a committee task group, is concerned with the selection of materials for valves, pumps and other equipment in the water industry. It is the desire of the parent committee to eventually cover all parts of the utility field, the electric and gas utilities as well as water.

### Poor Selection of Materials

In the general discussion, it was brought out that poor selection of materials and bad design cause corrosion problems. Use of devices having steel bolts with brass nuts, "a beautiful setup for corrosion" were cited. It was pointed out that specifications changes made on paper before installation can drastically cut down on replacement expense and problems. Design men often never know whether their designs are performing satisfactorily, it was stated.

One person said manufacturers can design high quality devices, but economy minded customers do not want to pay the price. As an example of this he cited the use of cheaper cast iron in gate valves to save money. He said most users want the cheapest valve possible.

### Low Cost Coating Sought

The American Water Works Association would like to check and certify valves, it was stated. The AWWA is seeking a low cost high performance coating. A sample of epoxy coating was passed around to persons in the group. It was pointed out that galvanizing would not work and no type of metallizing tried so far has been successful. Epoxy coatings had been tested up to three years with varying results. A catalytic type coating was found to be very tenacious. Baked coatings are avoided because of cost.

Dezincification troubles experienced by the City of Los Angeles were described. Change to Colorado river water caused dezincification of valve stems. Materials with high zinc compositions deteriorated rapidly with tuberculation

(Continued on Page 68)

## Tape Committee Holds Sessions at 3 Regional Meetings

Technical Unit Committee T-2K on Prefabricated Plastic Film for Pipe Line Coating will meet at three NACE Region Conferences this Fall. Meetings have been scheduled for the Northeast Region Conference, Boston, October 5-8; the North Central, Cincinnati October 15-17; and the South Central, New Orleans, October 20-24.

Principal business at the San Francisco meeting was hearing the reports of task groups T-2K-1 on Standards, T-2K-2 on Research and Development and T-2K-3 on Coating Evaluation.

Concerning T-2K-1, tentative recommended specifications and practices for prefabricated plastic films for pipe line coatings will be released for publication to members of the committee only as minimum descriptive standards, and will be submitted for approval to members of Committee T-2K at the next regional meeting, the committee decided. Work on the specifications had been furthered at the Oklahoma City meeting, H. D. Segool, chairman said.

### New Assignment Sought

Task Group T-2K-2, Research and Development, had no specific report to make, but requested the committee to review the assignment given it. The original assignment was stated by one person present as: "To study prefabricated plastic films available now as they are discovered in the laboratory paying particular attention to the plasticizers used to eliminate the possibility of a cheap plasticizer causing a breakdown of an otherwise good film with recommendation to both manufacturers and corrosion engineers, to study the moisture vapor transmission and chemical resistance, etc. of plastic films."

R. B. Bender and H. A. Hendrickson were appointed to study possible expansion of the group's assignment. They are to present recommendations at the next regional meetings for discussion and final approval at the 15th Annual NACE Conference.

It was suggested that the National Bureau of Standards be contacted for assignment suggestions. One person offered procedures used by his company for testing prefabricated plastic films. Because of the interest shown, the information will be mailed to all members present.

### Report on Use Discussed

Task Group T-2K-3 on Coating Evaluation discussed what has been done concerning the questionnaire the group mailed out. A consolidated report of information received up to March 1, 1958 from the questionnaire was presented. More information has been received since that time, it was stated. It was the opinion of the committee that many companies using plastic films have not received the questionnaire.

The chairman also reported that a permanent file has been set up for all installations that will require follow-up. These installations will be listed as projects. As of March, there were 17 projects listed.

It was decided not to distribute the consolidated report, but that another consolidated report will be made available for the next committee meeting.

The following procedure for handling the questionnaire was decided upon: Questionnaires will be mailed by NACE Central Office to all corporate members and T-2K committee members. The completed questionnaires will be returned to Central Office then forwarded to the chairman of the coating evaluation task group.

## Long Range Evaluation Of Plastic Tape Planned

A questionnaire has been prepared by Technical Unit Committee T-2K on Prefabricated Plastic Film for Pipeline Coating to gather data for long range evaluation.

The History and Results Subcommittee of Unit Commitee T-2K has been organized to give a long range study of actual installation of prefabricated plastic films on pipelines, the purpose being to gather data and making excavations to determine true values of plastic coatings and to maintain long range records of installations. The necessity to gather this long range data is created in companies when personnel who make an installation are promoted or transferred and the follow-up data or evaluation over the years is lost. The T-2K Committee is a permanent committee of NACE with the organization to follow up these installations and preserve long range test data results which will be valuable in years to come.

Any one interested in this problem may obtain copies of a questionnaire from NACE Central Office, 1061 M & M Building, Houston 2, Texas.

## Rectifier Ripple Inquiry On Agenda of T-4B-2A

Circulation of a questionnaire on filtering the rectifier ripple is being undertaken by Project Group T-4B-2A. The group is working under Unit Committee T-4B on Corrosion of Cable Sheaths. The group met in San Francisco, March 18. Work on the questionnaire was interrupted by death of the chairman. A new chairman was appointed to pick up the work.

Under "old business" a discussion of duct anodes was renewed. A report was made on New Jersey Bell Telephone Co. installations concerning six strings installed, one location with two strings with a large current output. Inspection showed anode deterioration which was not serious.

One telephone corrosion engineer told of the removal and inspection of two strings of graphite anodes in Pennsylvania. Graphite was deteriorated in spots, some badly. Other points developed in the discussion of graphite anodes were: Header wire separating from the anodes, extensive through uniform deterioration of anodes and the need for limitation of amount of current where graphite is attacked by acids.

The question of use of graphite anodes by power companies was brought up. Two firms were suggested as being possible sources of information. One engineer said he would not use a duct for lead cables after the duct had graphite residue in it from anodes.

## New Questionnaire Given To Cable Sheath Group

A newly devised questionnaire designed to help Project Group T-4B-5B in its work was presented to members of the group for their consideration at the San Francisco meeting, March 18. T-4B-5B on Practices and Experience with Protective Jackets for Outside Plant Communications Cables, is part of Unit Committee T-4B on Corrosion of Cable Sheaths. A copy of the questionnaire was appended to minutes of the meeting.

Another project group, T-4B-5A on Practices and Experience with Protective Jackets for Outside Plant Power Cables met preceding the T-4B-5B meeting. The presiding officer read a report on the project.

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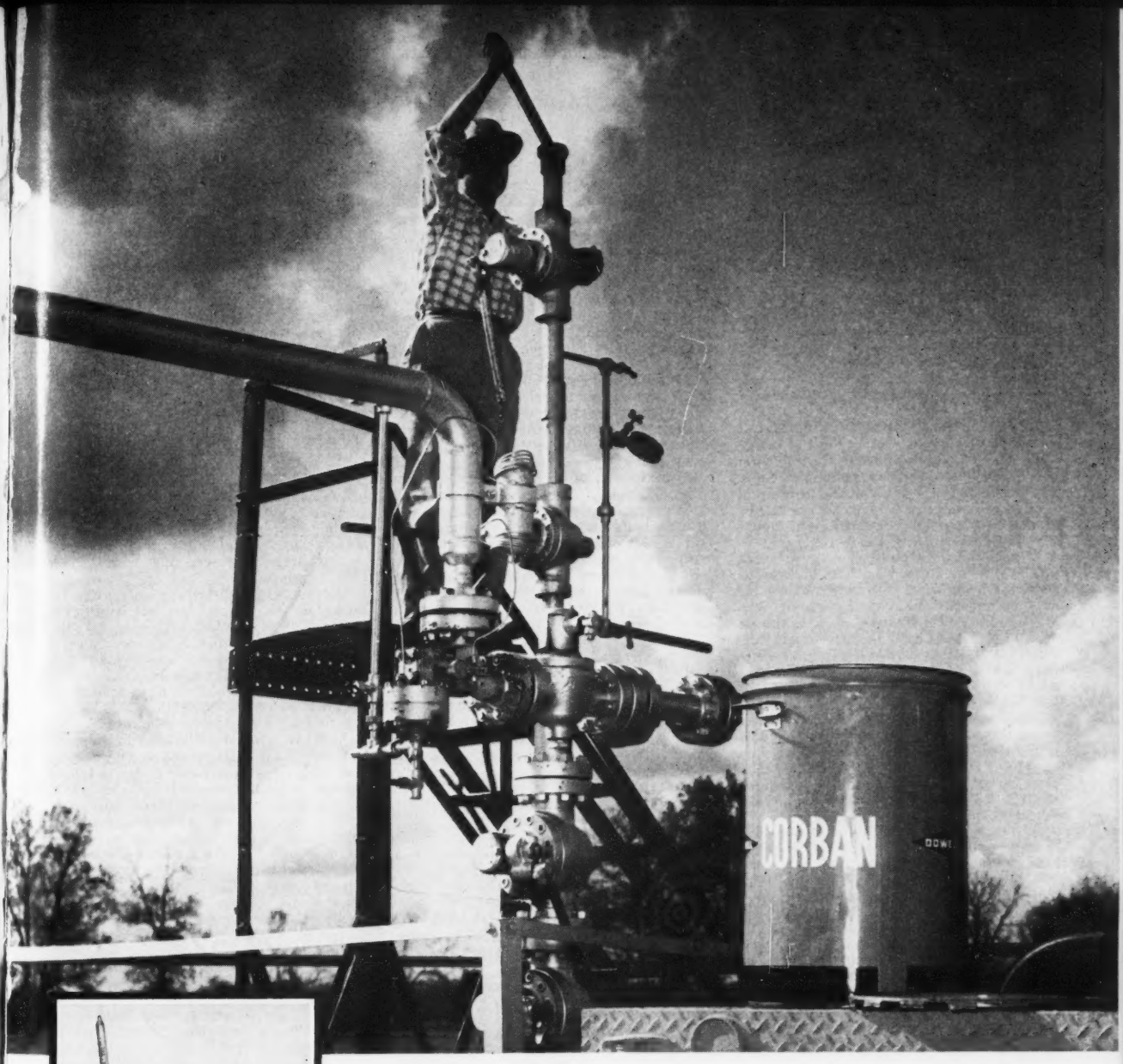

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## Discussion of Zero Resistance Ammeter Held by Group T-4B-3

Task Group T-4B-3 on Tests and Surveys, working under unit committee T-4B on Corrosion of Cable Sheaths, met in San Francisco, March 18.

There was a discussion of the development of the zero resistance ammeter concerning the possibility of incorrect readings due to contact potentials. Concerning duct anodes, one engineer pointed out that in a system at Peoria, Ill., two amperes were being discharged. Protection was limited to the manhole sections.

In a duct anode system in Buffalo, 2 amperes of current were required originally to bias lead cables to a potential of —0.85 volts. After isolating the cable sections, the same bias was obtained with 0.12 amperes. The zero resistance ammeter was used to determine the current on each cable.

Other miscellaneous points brought out at the meeting were: In answer to a question on what is considered a hazardous current loss on cables, it was stated that 35 ma loss in a manhole section is considered hazardous; in another case, tests showed that interference on a water pipe developed at a point anode amounted to 95 percent of the rectifier output.

Effect of moving a point anode away from the structure to be protected was illustrated on a curve presented by one engineer. He also suggested interference tests be made before ground beds are installed, to eliminate construction expense if they have to be moved.

A description of a test on a 500-foot section of coated gas pipe using magnesium anodes was presented.

One person emphasized that any protective system applied to an underground structure causes interference to adjacent underground structures and for that reason, an interference test should always be requested.

## More AC Corrosion Reports Are Given

Rates of corrosion due to alternating current and examples of AC corrosion were given at the meeting of Project Group T-4B-1B, To Develop Information on Galvanic Action, held in San Francisco, March 18. The project is part of Unit Committee T-4B on Corrosion of Cable Sheaths.

Some of the points brought out were: According to the Bureau of Standards, AC current will corrode metals at from one to two percent of an equal DC current. In a pipe line failure in the Jersey meadows, the potentials, pipe-to-ground were 10 V AC, 0.1 V DC, with the AC current 20 times that of DC.

Results of a simulated field test conducted by one firm with copper and aluminum indicate that the 60 cycle AC corrosion rate of aluminum is 33 percent of the DC rate. No figures were given for copper.

A letter from Great Britain requesting information on AC corrosion had been answered by one member of the group who described some corrosion experiences in which AC was believed to be a major contributing factor.

## Copying of Coordinating Committee Maps Weighed

The Chicago Area Committee on Underground Corrosion, a subcommittee of Unit Committee T-7B, North Central Region Corrosion Coordinating Committee reported on committee work at a meeting held April 15 in Hammond, Ind.

A lively debate was held on whether to comply with requests by an outside agency for copies of the committee's maps of underground facilities. The chairman was empowered to write a letter to member companies whose installations are shown on the map, asking their permission to release the map.

Much of the time was spent in exchanging information between corrosion engineers of different companies on work being done. In each case, specific information was given as to the location of work being done and what was being done. Installation of rectifiers and ground beds on pipe lines, drainage ties and a drainage survey were all dealt with specifically. One firm returned committee maps on which was overprinted the route of their 14-inch pipe line. The route of the line was then entered on the committee master map.

As a brief technical program, four persons present gave a demonstration of diodes used in cathodic protection systems.

Next meeting of the committee will be September 16, at the Peoples Gas Building, Chicago, at 1:30 pm.

## HF Alkylation Query Data Are Summarized

A report summarizing results of a questionnaire sent to the petroleum industry on problems in HF alkylation was reviewed at a meeting of Task Group T-5A-6 Corrosion in Hydrofluoric Acid on March 17 at San Francisco. This report is being processed for publication.

The group also discussed the bibliography of HF corrosion, now under review and problems with O-ring seals on HF pumps. F. H. Meyer discussed his paper on corrosion problems associated with uranium refining presented at the conference.

Additional information on construction materials for handling 10 percent HF solutions and means of disposing of the acid were sought. The corrosion problem of the refrigeration industry in heat exchangers using Freon containing azeotropic mixtures of up to 50 ppm chloride in water in the regrigerant was mentioned.

## Stray Current Inquiry

A summary of replies to a questionnaire was the principal subject considered at the meeting of Task Group T-4B-6 on Stray Current Electrolysis. The meeting was held in San Francisco, March 18, during the NACE 1959 Conference.

The questionnaire covered two categories, one on electric power cable practices and the other communication cable practices. A. F. Minor was appointed to head the group after the death during the year of M. B. Hart, who was chairman.

## Redox Interpretation Topic of Discussion

Task group T-4B-1D To Investigate and Develop Technical Information on Corrosion by Microbiological Action met in San Francisco to receive information collected on this subject since the progress report of March 1956. Another report on Interpretation of Redox Potentials was discussed at the meeting.

One member asked what protection could be used to combat biological attack. Answer was use of a cathodic protection system. The meeting was held March 18 as part of the meeting of Unit Committee T-4B on Corrosion of Cable Sheaths.

## Water Industry –

(Continued From Page 65)

in valves. In examining this problem, the role of oxygen starvation was studied, bronzes and stainless steels were tried. Nickel alloy stems are providing better service, but at a higher cost, it was said.

Valves with all-bronze interiors are doing a "fair" job, but all aluminum bronzes show crevice corrosion rapidly, and give off aluminum oxide. Several types of coatings on cast iron were tried, and use of epoxy resins is being studied. Los Angeles is now testing 50 different pieces of equipment and is trying to find a satisfactory coating.

Another discussion concerned use of butterfly valves. In one case, a corrosion check showed corrosion at the edge of leaves, probably caused by cavitation. New equipment is metallized with lead before service, but corrosion was believed caused when the lead is pushed aside by velocity. As a remedy, stainless steel (hot spray) over the entire leaf, followed by a coating of red lead is being tried.

One member spoke on stainless steel stems on valves. He persuaded manufacturers to change to ductile iron trim and one firm did not increase the price for the change, he said. He explained his own company was now using more butterfly valves because they have fewer moving parts and can be adapted to motor control. In flocculators using high silicon anodes with impressed current are being used on the paddles. The rectifiers are producing 12 amperes at 60 volts.

After some discussion, the decision was made for the group to approach the AWWA valve committee for aggressive water specifications. It was suggested that NACE have a representative at the AWWA meeting in Dallas.

Concerning flocculators, one person pointed out that they are made of a number of different metals. To prevent corrosion an attempt was made first to use magnesium anodes, and later impressed currents were used. It was suggested that metal and concrete should be insulated from each other.

Other corrosion information was exchanged at the meeting. Some of these were, bolts used on cast-iron pipe, lining of pipe, steel couplings on cast-iron lines, copper troubles, insulating steel from cast iron and lining with concrete.

Storage water heaters were discussed and grounding problems were considered. Ground rods were reported failing near the surface of the earth in New York.

# NACE NEWS

# New Orleans Meeting Plans Are Completed

**SCHEDULE OF TECHNICAL MEETINGS AT NEW ORLEANS**

| Monday October 20 | Tuesday October 21 | Wednesday October 22 | Thursday October 23 | Friday October 24 |
|---|---|---|---|---|
| **Morning—9 to 12** | | | | |
| T-1<br>T-2D<br>T-6A<br>T-3D-1 | T-8A<br>T-1B<br>T-1M<br>T-2J<br>T-6A-17 | T-8<br>T-6D<br>T-1D (9 am)<br>T-1H (10 am)<br>T-1K (11 am) | Refinery & Chem. Process Industries (Part 1)<br>Oil & Gas Prod. (Part 1) | Offshore Corrosion<br>Pipe Line |
| **Afternoon—2 to 5** | | | | |
| T-1<br>T-6B<br>T-2K | T-8<br>T-1C<br>T-1J<br>T-1F | Free Time for Visiting Exhibits | Refinery & Chem. Process Industries (Part 2)<br>Oil & Gas Prod. Symp. (Part 2) | |

## SOUTH CENTRAL REGION ABSTRACTS

### *Oil and Gas Production Symposium Part 1*

J. L. BATTLE, Humble Oil & Ref. Co., Houston, Chairman
W. C. KOGER, Cities Service Oil Co., Bartlesville, Okla., Co-chairman

**A Laboratory Method for Evaluating Corrosion Inhibitors for Secondary Recovery** by T. R. Newman, National Aluminate Corp., Chicago.
A new test method is presented for evaluating corrosion inhibitors for secondary recovery systems. It is a recirculating system comprising a five gallon reservoir, a pump and a test cell. The test is characterized by its relatively high ratio of volume of water to surface area of metal exposed. A unique feature is the method used for holding the coupons in the flow of the water. A transparent Lucite cell holds the coupons so they are visible during the test.

Several common variables were studied. They are dissolved oxygen, $H_2S$, dissolved solids and pH. Corrosivity of a brine was found to be almost directly related to the dissolved oxygen level. It was found also that a high $H_2S$ system was not necessarily more corrosive than one having a low level of $H_2S$, but that the attack became more localized. The higher the $H_2S$ level, the higher the inhibitor level required to obtain an equivalent level of protection. The greatest effects of variations in dissolved solids are indirect. The solubilities of dissolved gases and organic inhibitors are inversely proportional to the level of dissolved solids. The variation of pH in the range from 5 to 8 did not affect the performance of a typical inhibitor in a system without $H_2S$. When $H_2S$ was present, the protection with this inhibitor dropped off slightly as the pH was lowered to 5.

This test method was used to evaluate a number of commercial water flood inhibitors. Experimental inhibitors were tested until one was found that exceeded the performance of those now being used. This one was tested in several floods and the excellent performance, predicted from the laboratory results, was confirmed.

**Correlation of Oil Soluble, Water Dispersable Inhibitors for Sweet Oil Systems** by C. C. Nathan, The Texas Co., Houston.

**Results of Mixed Sucker Rod String Testing** by W. B. Koger, Cities Service Oil Co., Bartlesville, Okla.

**Field Evaluation of Cathodic Protection of Casing by J. E. Landers, J. D. Sudbury, J. J. Lehman and W. D. Greathouse, Continental Oil Co., Ponca City, Okla.**

### *Refinery and Chemical Process Industries Symposium—Part 1*

W. L. VORHIES, Freeport Sulphur Co., Port Sulphur, La., Chairman
R. M. EELLS, Esso Standard Oil Co., Baton Rouge, La., Co-chairman

**Corrosion of Refinery Equipment by Aqueous Hydrogen Sulfide,** by R. V. Comeaux, Humble Oil and Refining Co., Baytown, Texas.
$H_2S$ corrosion problems at temperatures below 400 F in the presence of water are presented for a wide range of refinery equipment. The most commonly accepted solutions to the problems of corrosion and fouling are the use of resistant alloys and/or neutralization plus film-forming corrosion inhibitors. Experience at several units employing steel condenser tubes exposed to waters contaminated with $H_2S$ and other acids will be discussed. A theoretical study of the corrosion of steel in $H_2S$ solutions reveals that prevention of high velocity, low pH exposures should be an effective control measure. Analysis of several failures of steel-tubed exchangers are discussed in the light of additional improvements that may be possible in design and selection of materials. Preliminary tests indicate that zinc or aluminum coated steel tubes may be useful in this environment.

**Plastic Materials of Construction** by John J. B. MacKenzie, Haveg Industries, Wilmington, Del.

**Use of Silicone in Refining and Process Industries,** by M. H. Leavenworth, Dow Corning Corp., Dallas.
The background of the nature of silicone materials is explained. Some of the physical properties of silicone materials, are demonstrated, showing the high and low temperature properties and some of their other unusual characteristics. Emphasis is placed on coatings that can be used to protect materials against corrosion. The discussion on coatings includes resinous materials for high temperature protective coatings as well as release coatings for the treatment of pipes and other equipment that handle sticky products.

### *Oil and Gas Production Symposium Part 2*

**Well Completion and Corrosion Control of High Pressure Gas Wells,** by W. F. Oxford, Jr., Sun Oil Co., Beaumont, Tex., E. H. Sullivan, United Gas Co., Shreveport, La. and D. R. Fincher, Tidewater Oil Co., Houston.
Since 1950, the completion of the higher pres-

(Continued on Page 72)

## *Business, Social Events Listed for Regional Meeting*

Final arrangements and details are complete for the NACE South Central Region Conference and Exhibition, to be held in New Orleans, October 20-24. All events will be at the Roosevelt Hotel.

The Oil and Gas Production and Refinery and Chemical Process Industries symposia each will hold two sessions. Including technical committees, 24 technical meetings will be held at the Conference.

As part of the meeting, executives of the region will meet at the South Central Region Board of Trustees Luncheon to be held in the Orleans room, the Roosevelt Hotel on Thursday. The region's education committee will meet at a luncheon in the Gold Room Tuesday.

**Business Luncheon Wednesday**

The annual business luncheon will be held at noon, Wednesday in the Gold Room. Clayton Rand, nationally known speaker and humorist will address the group. Thursday and Friday, prior to symposia meetings, breakfast will be held for authors who will present papers at the symposia. Technical committees will meet Monday, Tuesday and Wednesday morning. Wednesday afternoon has been left free for visiting exhibits.

A reception and dance will be held in the International Room Wednesday evening from seven to nine. Music for dancing will be furnished by Frankie Mann's orchestra.

For the ladies a program of tours, a style show, a luncheon and a breakfast have been arranged. Ladies' headquarters will be in the Creole Suite of the Roosevelt Hotel and will be open all day Monday through Thursday. Coffee and rolls will be available.

On Tuesday ladies will meet at Brennan's for breakfast from 9:30 to 11:00. A walking tour of the French Quarter starts at Brennan's at 11:00.

Wednesday a sightseeing bus tour starts at the Roosevelt Hotel at 1:30 p.m. The tour will visit the Garden District, the Lakefront and other places of interest. It will end at 4:30 p.m.

**Ladies Program Extensive**

Thursday there will be noon luncheon in the University Room of the Roosevelt. Mrs. Reynick will give a talk on the Mardi Gras. Mardi Gras Belle gowns will be modeled.

On Friday ladies will board the yacht "Good Neighbor" for a tour of the Port of New Orleans. Since the capacity of the yacht is 75 persons, of necessity, ladies will be accommodated on a first come, first served basis.

In addition to the special program

(Continued on Page 72)

Battle

Comeaux

Davis

Duesterberg

Engle

Fincher

Floyd

Goodman

Grosz

Horst

Koger

Leavenworth

MacKenzie

Miles

Nathan

Newman

Oxford

Robinson

Rosene

Simons

Smith

Sudbury

Sullivan

Vorhies

# SOUTH CENTRAL REGION MEETING AUTHORS and OFFICIALS

**JACK BATTLE**—Supervising Chemical Engineer, Production Dept., Humble Oil & Ref. Co., Houston. Since 1933 he has specialized in the solution of oil production corrosion problems, he is active in NACE technical committees and in API, AIME and ACS. He was educated at Southern Methodist University and University of Houston.

**G. J. DUESTERBERG**—Is president of Plastic Applicators, Inc., Houston, a company which he organized in November 1945. He is engaged in the application of baked plastic coatings and rubber linings to tubular goods, tanks and equipment to serve the oil, chemical and food processing industries of the Gulf Coast and Southwest. Mr. Duesterberg received a BS in 1940 from New Mexico School of Mines, Socorro.

**J. P. ENGLE**—Dowell Division of The Dow Chemical Company of Tulsa. Mr. Engle is a graduate of West Virginia University, where he received a bachelor's degree in chemistry. He has spent ten years with Electro-Metallurgical Company, in laboratory control of production of various ferro alloys; six years with Babcock and Wilcox Company, Research and Development Laboratory, in studies of corrosion fundamentals and control; and five years with Dowell. His present position is Laboratory Group Leader in charge of technical service and development work pertaining to the chemical cleaning of industrial equipment. He is a member of NACE, ACS and ASTM.

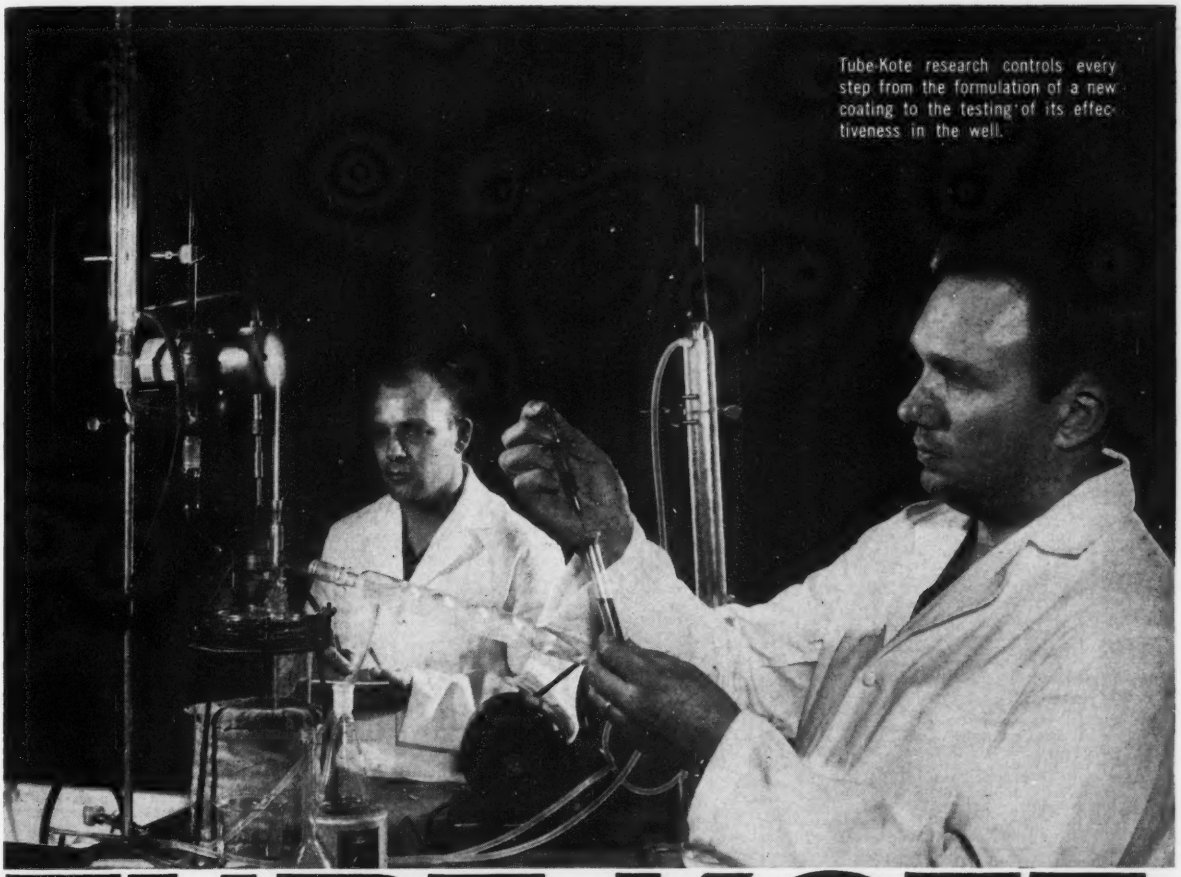
**D. R. FINCHER**—Is corrosion engineer for Southern Division of Tidewater Oil Co., Houston. He received a BS in chemical engineering from Texas A and M College in 1948. He was employed by Tidewater after graduation and has been active in corrosion work since 1949. He is chairman of NACE Unit Committee T-1B on Condensate Well Corrosion.

**G. L. FLOYD**—Dowell Division of The Dow Chemical Company, Tulsa. Mr. Floyd received a bachelor's degree in chemistry from the University of Oklahoma in 1952. Since that time he has been continuously employed by Dowell as a research chemist, working on problems related to corrosion inhibition and the chemical cleaning of industrial equipment. He is a member of The American Chemical Society.

**WALTON D. GREATHOUSE**—Is Group Supervisor, Production Chemistry Research, Continental Oil Co., Ponca City, Okla. He has had engineering experience in the processing of acid gases, in the transmission and combustion of natural gas, gas treating, in petroleum production chemistry. He graduated from Texas Technological College in 1937 with a BS in chemical engineering.

**O. L. GROSZ**—Since 1954 Mr. Grosz has been working as a corrosion engineer with The California Company, Harvey, La. He has a BS in mechanical engineering.

(Continued on Page 74)



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# SOUTH CENTRAL REGION ABSTRACTS

(Continued From Page 69)

sure gas wells has increased. The trend toward deeper drilling frequently has made necessary the production of gas wells with tubing pressures in excess of 5000 psi.

Corrosion problems associated with the higher pressure gas condensate production were, and are, of much concern to the operator. It was necessary to obtain higher strength materials in order to complete the higher pressure wells. Some operators indicated a desire, or preference, to change well completion practices. It was not known if inhibitors, coatings, and other protections used effectively in the lower pressure wells could, or would, perform adequately in the deeper wells with greater temperature and pressure. It was anticipated that corrosion would be a problem in most if not all of these "super" high pressure wells.

NACE Committee T-1B appointed a Task Group in early 1957 to study the problem. The scope of this group was to investigate and study completion practices and corrosion control means and measures concerned with gas wells with tubing pressures in excess of 5000 psi. A survey of producing companies was made to determine what had been done to combat the problem. This paper reflects the results of this survey.

**Polyurethanes—Plastics With an Oil Field Promise** by B. P. Goodman, Tube-Kote, Inc., Houston, Tex.

Although urethane chemistry is over one hundred years old, being one of the first of the organic chemicals to be synthesized, the urethanes are new to most people in the plastics field. Primary application of these materials to this field was done by the Germans during World War II. As German wartime developments were reviewed after the war, it was obvious these materials showed great promise for use in American industry.

The key to urethane plastic chemistry is that of polymer building through the mechanism of reacting an isocyanate group (—NCO) with another molecule of some sort containing one or more reactive hydrogens. The list of available compounds for this reaction is great; therefore, a high degree of versatility is possible in this new plastics field. By changing the nature of the reacting compounds, it is possible to obtain foams, rubbers, adhesives and coatings having any degree of flexibility or rigidity.

While room temperature reacted urethane coatings are gaining importance, they have exhibited certain application disadvantages such as low tolerance for moisture and toxicity. These disadvantages have been overcome using a baking-type "blocked" isocyanate. The baking-type coating, while necessarily limited to specialized application, has the advantages of improved chemical resistance and adhesion coupled with excellent hardness and flexibility. Both laboratory and field testing of this coating material have proved it to be a very important and highly successful addition to the field of chemical resistant plastics.

Because urethane chemistry is new and highly versatile, the future of this material in the fields of material design and corrosion control holds great promise.

**Testing Methods and Apparatus to Determine Coating Suitability for Oil and Gas Well Tubing** by G. J. Duesterberg, Plastic Applicators, Inc., Houston.

In formulating a suitable coating for "in the hole" tubular goods conditions that must be taken into consideration include elevated temperatures and pressures, corrosive liquids and gases that occur naturally in oil and gas wells and chemicals that are introduced into the wells during completion, such as caustics. Also conditions of physical abuse such as wire line work, distortion and elongation must be considered.

Various laboratory testing methods simulating actual operating condtions to determine coating suitability are discussed.

## *Refinery and Chemical Process Industries Symposium—Part 2*

**Application of Glassed Steel Equipment in Corrosive Service**, by R. E. Smith. The Pfaudler Co., A Div. of Pfaudler Permutit, Rochester, N. Y.

The corrosion resistance of glassed steel is discussed. Other properties of practical interest are reviewed briefly, including resistance to thermal and mechanical shock, absence of catalytic effects, anti-adhesion, cleanability and repairability. A brief description of the manufacturing process is related to design considerations. Finally an illustrated series of operating industrial installations of glassed steel equipment are presented as examples of the use of the foregoing properties.

**Chloride Stress Corrosion Cracking of the Austenitic Stainless Steels** by J. P. Engle, G. L. Floyd, R. B. Rosene, Dowell Div., The Dow Chemical Co., Tulsa, Okla.

The austenitic (AISI 300 series) stainless steels are highly subject to chloride stress corrosion cracking. This work was undertaken to define conditions under which hydrochloric acid can be safely used for chemically cleaning equipment containing these steels.

The active-passive characteristics of the alloys play an important role which probably has not been understood previously. A number of factors, acting together, must be present to produce cracking. Indications are that cracking occurs in neutral chloride solutions, when passivity is destroyed at localized areas of film break-down. If the entire surface is activated, as in the presence of hydrocholoric acid, no cracking will result.

The data were obtained by tests on horse-shoe type specimens, statically stressed to 75 percent of yield strength. Specimens in the annealed, cold rolled and sensitized condition were used to simulate conditions likely to be encountered in alloys in the "as fabricated" condition. Exposures were made in 5 percent hydrochloric acid solutions to simulate cleaning conditions. Other tests were made in dilute neutral chloride solutions at 400 F to simulate operation after cleaning.

The problem of design is considered, as is proper selection of alloy types, especialy if welding is to be performed during fabrication.

**Nickel Extraction by the Moa Bay Process—A Problem in Materials Selection** by C. S. Simons, Chief Process Engineer, Cuban American Nickel Co., New Orleans.

A brief description of the Moa Bay process to be used by Cuban American Nickel Company (a Freeport Sulphur Company subsidiary) to extract nickel and cobalt from the lateritic iron ores of Moa Bay, Cuba, is given. The high-temperature, high-pressure acid leaching step, the heart of the process, is described in detail. The many problems in design, materials selection and fabrication methods involved in applying the leaching step on a large scale are discussed and the final solution of these problems (vessel design, piping, heat exchange, acid injection and pressure letdown) are indicated. Some data on specifications are presentd.

## *Offshore Corrosion Symposium*

O. L. GROSZ, The California Co., Harvey, La., Chairman

C. L. BARR, Shell Oil Co., New Orleans, Vice-chairman

**Offshore Coating Application Developments** by Jack Eggleston, Vapor Honing Company, Inc., Houston, Tex.

A 12-year progression is given of a new industry relating the developments of materials, equipment, techniques, labor and economics for coating offshore installations. Interrelationship between manufacturers, applicators and customers will be discussed and various past and present co-ordinated factors that can produce the optimum in corrosion control offshore will be considered. Various methods of letting contracts for applicators and related problems that can result will be pointed out. A description will be given of today's offshore coating applicator. A brief discussion of existing maintenance contracts with initial problems and various developments that have occurred in three years with two major oil companies is included. Developments related to economics of offshore drilling and how these factors have cause and effect relationship with the costs of applications offshore are discussed. Forecast of the future for offshore coating applicators is made.

**Paint Maintenance on Offshore Equipment** by R. M. Robinson, Continental Oil Co., Houston.

**Aluminum Anodes for Cathodic Protection**, by R. L. Horst, Jr., Aluminum Company of America, New Kensington, Pa.

Development of the aluminum anode alloy is described and several examples of cathodic protection with aluminum anodes are given. The comparative values of aluminum to other metals as a galvanic anode material are discussed.

## *Pipeline Symposium*

MARION FRANK, Tennessee Gas Transmission Co., Houston, Chairman

DEAN GRIFFITH, Shell Pipe Line Co., Houston, Vice-chairman

**Sacrificial Anodes for Submerged Pipelines** by Robert G. Ransom, Tennessee Gas Transmission Co., Houston.

System expansion into offshore areas for gas supply requirements presented hithertofore unencountered problems in regards to maintenance of a submerged pipeline.

Protective requirements for offshore sections of the line remote from practical sources of impressed protective current and subject to irrepairable coating damage during installation dictated use of a large amount of sacrificial anode material. Inaccessibility of the line after laying meant reliability and long life were paramount design factors.

Pipelaying methods employed required no projections beyond the surface of the concrete weight coating and an essentially uniform line surface was necessary.

An anode design evolved consisting of a sleeve or bracelet of material replacing a portion of the weight coating on certain joints of pipe.

The bracelet of anode material consisted of anode sectors assembled into an annular ring about the pipe using a circumferential steel band at each end for support. Pipeline design with the working pressures involved prevented any direct welding of the assembly to the pipe itself.

Anode material requirements included resistance to passivity in seawater, good current efficiency, relatively low driving potential and molding considerations for the anode sector shape employed.

Because of the low electrical resistivity of the environment, current distribution aspect was considered secondary to a standardized spacing for the pipelaying job. Then an anode length was determined to provide the necessary anode material for the protective requirements.

Experience gained with the completion of the first installation of 26-inch pipe has materially aided in the design of assemblies for subsequent pipeline installations of various diameters.

**Development and Evaluation of deep ground beds**, by Paul Miles, Corrosion Group Leader, Interstate Oil Pipe Line Company, Shreveport, La.

An economical method of applying cathodic protection to bare pipe lines in high resistance soil has been found. Interstate Oil Pipe Line Company is now using 250-foot vertical anodes with unusual success. This paper deals with the development, design, installation, performance and cost data of such groundbeds.

**Corrosion Control on Aerial Pipe Line Crossings** by Gordon O. Davis, Transcontinental Gas Pipe Line Corp., Houston.

## New Orleans Meeting—

(Continued From Page 69)

planned for them, ladies also are invited to the reception and dance Wednesday, 7-9 p.m. in the International Room of the Roosevelt. Frankie Mann's orchestra will play.

All charges for ladies' activities are included in the $7.50 registration fee.

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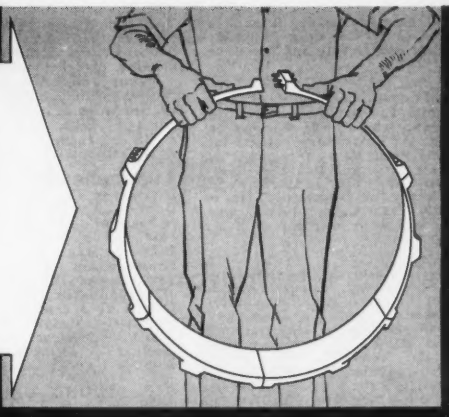
Bibliographic Surveys of Corrosion published by NACE now cover the years 1945-53 inclusive.

### SINGLE COPY PRICES OF CORROSION INCREASED

Effective at once the price of single copies of CORROSION to members of the National Association of Corrosion Engineers will be $1 each. The price of single copies to non-members of NACE will be $2 each.

For issues dated two or more years past (i.e. all issues dated 1956 or earlier) the price per copy is $2 to members and non-members alike.



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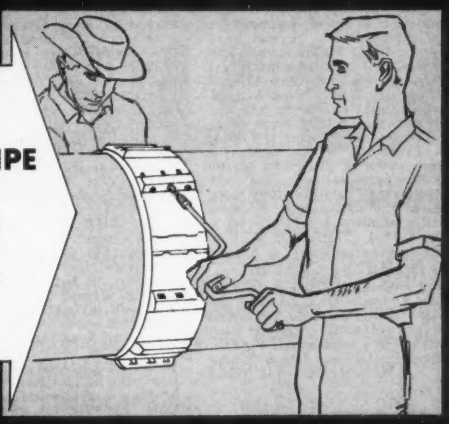

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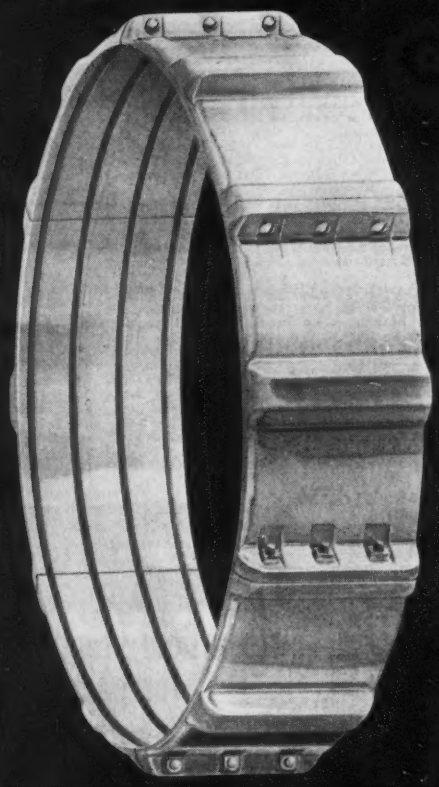
TIGHTEN 3 LARGE BOLTS

IT'S A 'SNAP' FOR BIG-INCH PIPELINES



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# SOUTH CENTRAL REGION BIOGRAPHIES

(Continued From Page 70)

**R. L. HORST, JR.**—Graduated from Columbia University in 1948 with an MS in chemical engineering. He joined the sales development division of the Aluminum Company of America where he has been concerned with a variety of corrosion studies. Mr. Horst has published articles on cathodic protection, aluminum and magnesium anodes and aluminum alloy applications in the chemical and processing industries. He is a member of NACE.

**W. C. KOGER**—Cities Service Oil Co., is head of the corrosion and oil treating section, oil production division, Bartlesville, Okla. He has been with Cities Service since immediately after his graduation from the University of Arkansas with a BS in chemical engineering in 1944. His first assignment was refinery research. In 1946 he was transferred to the company's oil production division as corrosion engineer in the West Kansas division. Mr. Koger is vice chairman of NACE Technical Committee T-1 on Oil String Casing Corrosion, West Kansas Area. He is also a member of three other working NACE technical committees. He is the co-chairman for the Oil and Gas Production Symposium for the 15th Annual NACE Conference.

**J. E. LANDERS**—Is associated with Continental Oil Co., Ponca City, Okla., with a break of two years for military service from 1955-57. He is a graduate of Southern Methodist University. He joined NACE while a student.

**M. H. LEAVENWORTH**—Has been with Dow Corning Corp. since 1945. He opened the firm's Southwest branch office in Dallas in January 1948 which he has headed since that time. Mr. Leavenworth joined the firm's sales force in 1946 and served as a technical representative in the state of Michigan. During World War II he was an instructor in aircraft maintenance for Navy personnel at Norman, Okla. and for the Army Air Force at Willow Run, Mich. He has a BS from Eastern Michigan College, graduating in 1939.

**JOHN J. LEHMAN**—Is district engineer for the Continental Oil Co., Plainsville, Kans. He has been a member of NACE since 1956. He has a BS in chemical engineering and has done graduate study.

**C. C. NATHAN**—Is research chemist at Texaco's Exploration and Production Research division, Bellaire, Texas, where he is working on corrosion inhibition. He holds three patents for developments in this field. He is the author of technical articles on corrosion and is a graduate of Rice Institute and received his MS and PhD at the University of Pittsburgh. He is chairman of NACE Task Group T-1K2, vice chairman of T-1K and is a member of T-1C and T-1D.

**T. R. NEWMAN**—Is Research Chemist, Physical Chemistry Laboratories, National Aluminate Corporation of Chicago. Mr. Newman received a BS in chemistry from the University of Chicago in 1949. He joined the National Aluminate Corporation in 1949 and has been with them since. Mr. Newman's fields of research have included coagulation, corrosion and analytical techniques. For the past several years his work has been concerned with corrosion in aqueous systems.

**W. F. OXFORD, JR.**—In the Corrosion Analytical Group, Production Research Laboratory, Gulf Coast Division, Sun Oil Co., he was head of the firm's section in 1955. He is engaged in oil and gas condensate well corrosion problems and salt water disposal studies. Mr. Oxford received a BS in chemistry from Texas A & M College where he also taught chemistry and did graduate work. A member of NACE since 1950, he has been vice chairman of Technical Group Committee T-1 on Corrosion in Oil and Gas Well Equipment and was vice chairman of the Oil and Gas Production symposium for the 1955 annual NACE Conference. The followinng year he was co-chairman of the symposium. He is a member of technical committees T-1B, T-1B-1, T-1C, T-1H, T-1M, T-5C-1, T-1K and T-1K-3.

**ROBERT M. ROBINSON**—Is Senior Production Engineer with Continental Oil Co., CATC Marine Region, New Orleans Division. He has been with Continental Oil Co. since 1954 and has been concerned with offshore corrosion control since that time. He is a member of NACE, past chairman of the New Orleans-Baton Rouge Section, past chairman of Group Committee T-1M on Offshore Corrosion and was co-chairman of the Marine Symposium for the 1957 South Central Region Meeting. He is also a member of other technical committees.

Before joining Continental Oil Co., Mr. Robinson was with Shell Oil Co. in 1950. He worked on corrosion mitigation in Kansas and Oklahoma oil fields until 1954. He graduated with a BS in chemical engineering from Texas A & M and received his MS in 1950.

**R. B. ROSENE**—Laboratory Director, Dowell Division of The Dow Chemical Company, Tulsa. Born in Novelty, Wash., Dr. Rosene received a bachelor's degree from Whittier College in 1944 and a PhD from Purdue University in 1951. He was research chemist for the Plantation Division, U. S. Rubber Company on its Far Eastern Plantation in Sumatra, Republic of Indonesia in 1951 and 1952. He then joined Dowell as a research chemist and was shortly thereafter promoted to group leader. He attained his present position as laboratory director in 1954. He is a member of Sigma Xi, Phi Lambda Upsilon and ACS.

**C. S. SIMONS**—Has been associated with the development of the Moa Bay process since its inception in 1952. He directed the early investigations, carried out at Freeport Sulphur Company's Hoskins Mound, Texas, property and moved to New Orleans as chief process engineer when the pilot plant stage of development was reached. He is author or co-author of a number of patents (issued and pending) covering process and equipment involved in the development. Mr. Simons received his primary education in the Houston public schools and received the degree of bachelor of science in chemical engineering from Rice Institute in 1940. He has seventeen years service (including a four year leave-of-absence for Army service in World War II) with Freeport Sulphur Company and its subsidiaries.

**J. D. SUDBURY**—Is research group leader, Development and Research Department, Continental Oil Co. He holds a PhD in physical chemistry, University of Texas, 1949. He is a member of NACE and other engineering organizations and for the past nine years has been active in oil well corrosion research. He is the author of many papers on corrosion control. He is a member of six NACE technical committees.

**E. H. SULLIVAN**—United Gas Pipe Line Co., has been a member of NACE since 1945 and has been active in corrosion work since that time. In 1957 he was chairman of Shreveport Section NACE and was active in technical committee T-1. He presently is a member of technical committees T-1B, T-1B1, T-1C and T-1M. He graduated from Texas A & M College in 1939 with a degree in engineering administration. He is a registered Texas professional engi-

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## Mailings Planned for Western Region's Nov. 17-21 Meeting

Officials of the Western Region 1958 Conference are conducting a publicity campaign for the region's Eighth Annual Conference and Corrosion Short Course, November 17-21 in Los Angeles. Three mailings will be sent out.

The first mailing in July listed symposia to be presented on corrosion in refineries, aircraft and missiles, food processing, marine environments, chemical processes, underground metallic structutures and petroleum production. It went to NACE members, prospective corporate members and a selected list of non-members.

The short course will be held during the last two days of the program. A demonstration type course, it will cover cathodic protection instruments and their use, surface preparation, application of coatings and paint and plastic coatings. Because the course will consist of field demonstrations, the number of persons attending will be limited to 100. All registrations must be made in advance with Frank V. Wilby, Southern California Gas Co., P. O. Box 3249, Terminal Annex, Los Angeles 54, Cal. The conference portion of the program will be held in the Statler Hotel.

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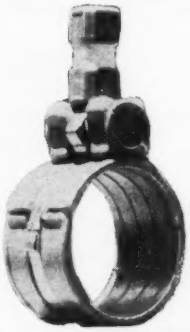

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A wide variety of corrosion information will be given in the 31 technical papers and two educational lectures comprising the technical program at the Cincinnati meeting of North Central Region in October. The papers, arranged in seven symposia and all social events will be at the Sheraton Gibson Hotel.

Hare

A social hour and banquet will be held on the evening of Thursday, October 16.

Seven technical committee meetings also are scheduled to be held.

The program follows:

Halbig

Falck

W. E. Hare, DBA-Hare Equipment, Cincinnati is general chairman; Sylvan B. Falck, Inner Tank Lining Corp., Cincinnati is technical program chairman and John Halbig, Armco Steel Corp., Middletown, Ohio is technical program committee vice-chairman.

### Wednesday, Oct. 15

#### Corrosion Problems in the Process Industries

Alfred D. Jenss, Ampco Metal Inc., Cincinnati, chairman.

Unusual Corrosion Problems, Mars G. Fontana, Ohio State University, Columbus.

Corrosion Problems in the Brewing Industry, Rudolph A. Bender, Jr., Bender & Assoc., Westerville, Ohio.

Copper Base Materials Corrosion Problems, Irving S. Levinson, Ampco Metal, Inc., Milwaukee, Wis.

Corrosion Problems in Nitric Acid and Ammonium Nitrate Industries, D. M. Carr, The Chemical and Industrial Corp., Cincinnati.

#### Stress Corrosion Cracking in Austenitic Stainless Steels

O. B. Ellis, Armco Steel Corp., Middletown, Ohio, chairman.

Statement of the Stress Corrosion Cracking Problem, Wayne Z. Friend, The International Nickel Co., Inc., New York.

Stress Corrosion Cracking of Austenitic Stainless Steels in High Temperature Chloride Water, Mars G. Fontana, Ohio State University.

Motion Picture: Showing Propagation of Stress Corrosion Cracks—Mars G. Fontana.

Observations on Stress Corrosion Cracking of Austenitic Stainless Steels, Walter K. Boyd, Battelle Memorial Institute, Columbus, Ohio.

Chloride Stress Corrosion Inhibitor Program, J. H. Phillips, National Aluminate Corp., Chicago, and W. U. Singley, Westinghouse Electric Corp., Pittsburgh.

Summary, Wayne Friend.

#### Educational Lectures

Chemical and Electrochemical Phenomena in Rocket Propulsion Applications, A. A. Watts, Aerojet-General Corp., Sacramento, Cal.

Useful Applications of Corrosion, F. S. Schultz, Malta Test Station, General Electric Co., Ballston Spa, N. Y. and A. E. Howe, General Engineering Lab. General Electric Company, Schenectady, N. Y.

### Thursday, Oct. 16

#### Corrosion Problems in The Nuclear Field

Fred H. Meyer, Jr., National Lead Co. of Ohio, Cincinnati, chairman.

Corrosion of Materials in Sodium, Lithium & Lead, W. D. Manly, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Corrosion Testing of the Zircaloys, Stanley Kass, Westinghouse Electric Corp., Pittsburgh

(Continued on Page 78)

## TECHNICAL PROGRAM

North Central Region Meeting

**CINCINNATI, OHIO—OCTOBER 15-17, 1958**

**Wednesday, Oct. 15**

**9:30 am-12 m**

Corrosion Problems in the Process Industries Symposium

Technical Committee Meetings: T-5B High Temperature Corrosion; T-3F Corrosion by High Purity Water

**2-4:30 pm**

Stress Corrosion Cracking in Austenitic Stainless Steel Symposium

Technical Committee Meeting: T-2K Prefabricated Plastic Film for Pipe Line Coatings

**4:45 pm**

Educational Lecture: Chemical and Electrochemical Phenomena in Rocket Propulsion Applications

**Thursday, October 16**

**9:30 am-12 m**

Corrosion Problems in the Nuclear Field Symposium

Technical Committee Meetings: T-7B North Central Region Corrosion Coordinating Committee; T-5A-4 Chlorine; T-6F Protective Interior Linings, Applications and Methods

**2-4:40 pm**

Protective Coatings, Inorganic Symposium

Corrosion Problems in the Utilities Industry Symposium

Technical Committee Meeting: T-5A-6 HF Corrosion

**4:45 pm**

Educational Lecture: Useful Applications of Corrosion

**Friday, October 17**

**9 am-12 m**

Protective Coatings, Organic Symposium

Developments in Corrosion Resistant Metals Symposium

# ged for Cincinnati Oct. 15-17

## TECHNICAL PROGRAM CHAIRMEN AND AUTHORS

Beck

Bender

Boyd

Carr

Denny

Ellis

Faust

Fink

Fontana

Friend

Frost

Galloway

Graham

Jenss

Kass

Kendall

Kretschmer

Levinson

Luce

Mackey

Manly

McVey

McDaniel

Meyer

Miller

Munger

Pelton

Phillips

Plankenhorn

Schultz

# Corrosion Resistant Metals Topic at Cincinnati

(Continued From Page 76)

Evaluation of Container Materials for Nuclear Fuel Recovery Processes, Paul D. Miller, Charles L. Peterson, Earl L. White and Walter E. Clark, Battelle Memorial Institute, Columbus

Evaluation of Materials of Construction for the Uranyl Ammonium Phosphate Uranium Recovery Process, Fred H. Meyer, Jr., National Lead Co. of Ohio, Cincinnati

A History of Corrosion Problems in the Plutonium Separation Process, Wm. L. Walker, General Electric Co., Hanford, Wash.

### Inorganic Protective Coatings

W. M. Spurgeon, General Electric Co., Cincinnati, chairman

Chromium as a Protective Coating, E. J. Seyb, Metal & Thermit Corp., Detroit

Precious Metal Plating and Corrosion, H. F. Smith, Smith Electrochemical Co., Cincinnati

Electrodeposited Alloy Coatings, C. L. Faust, Battelle Memorial Institute, Columbus

Flame Plating, J. F. Pelton, Linde Company, Indianapolis

Ceramic Coatings vs Metal Corrosion, W. J. Plankenhorn, Chicago Vitreous Corp., Cicero, Ill.

### Corrosion Problems in the Utilities Industries

W. J. Kretschmer, Columbia Gas System Service Corp., Columbus, chairman

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## TECHNICAL PROGRAM CHAIRMEN, AUTHORS

Seyb

Sims

Smith

Spurgeon

Watts

Soil Oxidation Reduction Potential Determination, Roger E. McVey, The Manufacturers Light and Heat Co., Pittsburgh

Plastic Coated Pipe, H. M. McDaniel, Republic Steel Corp., Cleveland, Ohio

The Use of Filming Amine for Prevention of Corrosion in Condensate Systems, Edward E. Galloway, Cincinnati Gas & Electric Co., Cincinnati

Glass Fiber Reinforcing of Coatings, B. A. Graham, L-O-F Glass Fibers Co., Waterville, Ohio

### Friday, Oct. 17
### Organic Protective Coatings

Sylvan B. Falck, Inner-Tank Lining Corp., Cincinnati, chairman

Structural Design and Corrosion, C. G. Munger, Amercoat Corp., South Gate, Cal.

A Classification of Protective Coatings According to Their Performance, Kenneth Tator, Kenneth Tator Associates, Coraopolis, Pa.

Practical Aspects of Protective Coating Specifications, J. R. Allen, and G. Mackey, E. I. du Pont de Nemours & Co., Wilmington, Del.

Acid Brick and Corrosion Resistant Mortars in Chemical Construction and Maintenance, Thomas E. Ronay, The Richardson Co., Melrose Park, Ill.

### Developments in Corrosion-Resistant Metals

F. W. Fink, Battelle Memorial Institute, Columbus, chairman

Some Recent Developments in Light Metals, P. D. Frost, Battelle Memorial Institute, Columbus

Uncommon Engineering Metals, L. F. Kendall, Jr. and John P. Denny, General Electric Company, Schenectady, N. Y.

Developments in High-Strength, Corrosion-Resistant Alloys, F. H. Beck, The Ohio State University, Columbus

Recent Developments in Oxidation Resistance and Protection of Refractory Metals, C. T. Sims, Battelle Memorial Institute, Columbus

New Developments in Heat Treatment Improve Corrosion Resistant Alloys, Walter A. Luce, The Duriron Co., Dayton, Ohio.

## Rectifiers Is Topic

At its August 5 meeting, Shreveport Section scheduled a talk by T. P. Wilkinson, the Holcombe Co., Shreveport. His subject was "Rectifiers for Cathodic Protection."

## NORTH CENTRAL REGION ABSTRACTS

### *Corrosion Problems in the Process Industries*

**Unusual Corrosion Problems** by M. G. Fontana

Problems different from "the run-of-the-mill" or ordinary corrosion problems are discussed and illustrated by black-and-white and color slides. Examples include unexpected failures and also problems difficult to solve. Chemical plant, oil refinery, petroleum production and other problems are described. Some of the information presented resulted from visits to offshore platforms in the Gulf of Mexico, the island of Aruba off the coast of Venezuela and the Dominican Republic.

**Corrosion Problems in the Brewing Industry** by Rudolph A. Bender, Jr.

Corrosion in a brewery can become an expensive factor, if conditions suitable for corrosion are not properly considered in design of equipment or operation thereof. The nature of the brewing process incorporates most of the elements for potential corrosion, but they can be minimized or entirely eliminated by the judicious choice of materials of construction and/or appropriate preventative measures.

Case histories of interesting phenomena that have occurred in recent years and the practical and successful counter-measures finally adopted are discussed. The fallacy of being too dogmatic in evaluating corrosion possibilities is demonstrated.

The increasing popularity of 'intensified' cleaning methods, favoring increased rates of corrosion, predicts the use of more noble metals of fabrication.

**Copper Base Material Corrosion Problems** by Irving S. Levinson

A review of the various types of corrosion problems that can occur in the process industries when using non-ferrous materials.

Case histories are given with remedial action taken, for problems with oxygen shielding, dezincification, de-aluminification, stress-corrosion cracking, velocity, cavitation and erosion, corrosion fatigue electrolytic corrosion, etc.

A detailed study of stress-corrosion cracking in aluminum bronze is described.

Consideration is given to various alloys in

(Continued on Page 79)

# NORTH CENTRAL REGION ABSTRACTS

(Continued From Page 78)

the copper-base field and the author's experience in getting the most out of each in given circumstances.

**Corrosion Problems in Nitric Acid and Ammonium Nitrate Industries** by D. M. Carr

In nitric acid plants, the problems and limitations are well defined and can be met by proper selection and heat treatments. Unless boiling acid is encountered, 304L, 321 and 347 maybe used without heat treatment; 304 and 430 maybe used with proper heat treatment. Carbon contents must be low. For applications above 250 F or with boiling, Duriron or tantalum must be used. Titanium may work. Condensation with subsequent evaporation is always bad.

Heat stresses often cause cracking, usually where design does not permit free expansion. This is especialy true in tube sheets.

Sometimes, cooling water with chlorides and other metals corrodes metal that withstands acids.

In ammonium nitrate solutions, aluminum is widely used. There are indications that it should be as pure as possible. Variations in analyses within the manufacturer's specifications have been giving trouble in three locations. Normally, the low magnesium alloys are considered satisfactory by the manufacturer.

## Stress Corrosion Cracking in Austenitic Stainless Steels

**Stress Corrosion Cracking of Austenitic Stainless Steels in High Temperature Chloride Waters** by Mars G. Fontana

Stress-corrosion cracking of austenitic stainless steels was studied under various conditions of tress, chloride concentration, complete immersion of specimens, intermittent wetting and drying and presence of oxygen. Stress-corrosion cracking will occur at stresses as low as 2000 psi at 50 ppm NaCl. A three-dimensional analysis of stress-corrosion cracks was made and a mechanism of cracking proposed.

A movie showing propagation of cracks at actual speed will be presented.

**Observations on Stress Corrosion Cracking of Austenitic Stainless Steels** by Walter K. Boyd

Case histories of a number of stress corrosion cracking failures encountered in plant service are presented and discussed. Emphasis is placed on the type, extent and frequency of the cracking observed. Research techniques employed to establish that the failure is one of stress cracking also are described.

**Chloride Stress Corrosion Inhibitor Program** by J. H. Phillips and W. J. Singley

A series of screening tests were run in tilting autoclaves to evaluate the performance of selected, potential inhibitors in preventing chloride stress corrosion attack of Type 347 austenitic stainless steel in alkaline-phosphate boiler water containing 50 or 500 ppm chloride. The tests were conducted at a temperature of 500 F and saturation pressure. On the basis of the screening test results, a number of the more promising inhibitors were tested further to evaluate concentration effects. Of the chemicals tested, nitrate appears to be a satisfactory inhibitor for boiler application. Sodium sulfite also effectively prevents chloride stress corrosion cracking by scavenging oxygen.

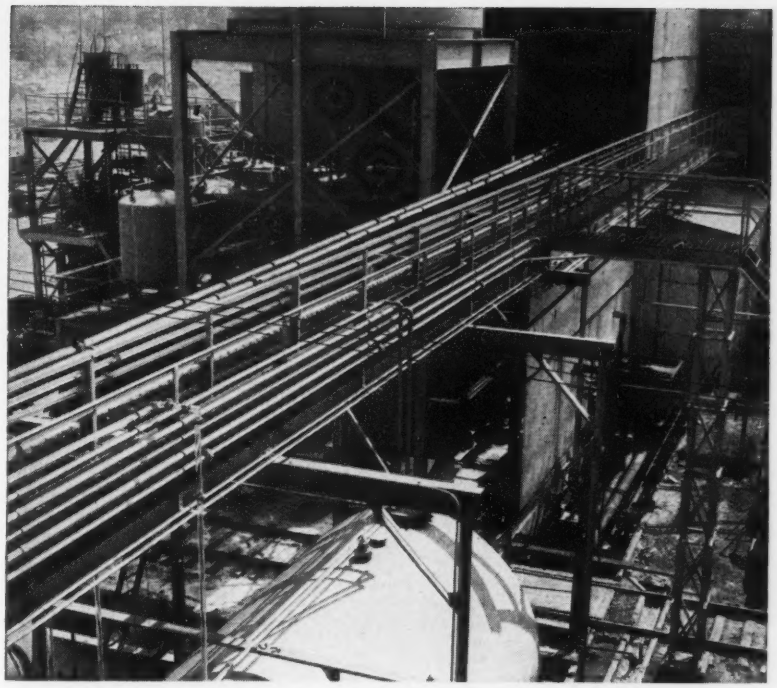
## Educational Lectures

**Chemical and Electrochemical Phenomena in Rocket Propulsion Applications** by A. A. Watts

The principles of electro-chemistry as related to corrosion and other electrochemical applications for rocket engine systems are reviewed briefly. Application of these principles is discussed with respect to corrosion of structural materials at low and moderately elevated temperatures by various rocket propellants such as nitric acid, hydrogen peroxide, nitrogen oxides, systems containing fluorine and chlorine and chemical fuels. Especial attention is devoted to chemical compatibility between materials and propellants.

Structural materials are exposed also to gaseous combustion products at high temperatures under high velocities and severe erosive conditions. The combustion gases may contain free oxygen and other reactive constituents. The extent of reaction or corrosion varies consider-

(Continued on Page 80)

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# NORTH CENTRAL REGION ABSTRACTS

(Continued From Page 79)

ably with environmental composition, which in turn is affected by time-temperature-pressure relationships. High-temperature corrosion rates are quite different in rocket combustion environments than in the combustion products of air-breathing systems.

Many other principles of electro-chemistry are utilized in the utilization of chemical milling, stripping solutions, electro-forming processes and deposition of electroless coatings. Electrode polarization studies can be very important in controlling reactions in these processes.

**Useful Aspects of Corrosion** by F. S. Schultz and A. E. Howe

In their constant fight to overcome or minimize corrosion, few engineers stop to think of the many useful aspects of corrosion which take place around us daily.

Controlled corrosion is used extensively for producing energy electrically, for cleaning metals and for metal removal processes. The latter use has grown into prominence in the last few years. Processes such as chemical milling, electrolytically assisted grinding and virtual electrode machining, which are all corrosion processes are revolutionizing metal machining operations. These processes, their application and limitations are discussed.

## Corrosion Problems in the Nuclear Field

**Corrosion of Materials in Sodium, Lithium, and Lead** by W. D. Manly

For the past several years the liquid metals sodium, lithium, lead and bismuth have been examined for possible use as heat transfer media in the various atomic energy programs. Many corrosion techniques and equipment have been developed during this time to study corrosion by these unique coolants. It has been found that liquid metal corrosion is mainly a solution phenomenon. The effect of impurities, temperature, temperature gradient and flow velocity on the corrosion mechanism has been examined and will be presented in this paper. Temperature gradient mass transfer and isothermal mass transfer (dissimilar metal transfer) will be discussed.

It has been found that sodium is compatible with most constructional alloys of the cobalt-base, nickel-base or iron-base type. Lithium and lead are more difficult to contain and only materials such as pure iron, iron-base alloys, 400 series stainless steels, molybdenum, tungsten, columbium and tantalum show much promise as containers. In these environments the austenitic stainless steels and nickel-base alloys are severely corroded.

**Corrosion Testing of the Zircaloys** by Stanley Kass

Zircaloy-2 and Zircaloy-3 have found extensive application in water cooled and moderated reactors due to their excellent corrosion properties in high temperature water and steam. These excellent corrosion properties are inherent in the alloys; however, the corrosion behavior in pressurized high temperature water and steam is greatly influenced by sample preparation and the manner in which the test is conducted. This paper is concerned with the external factors influencing the corrosion behavior of the Zircaloys. These factors include sample preparation and identification, cleaning, etching and rinsing, as well as test equipment and procedures.

**Evaluation of Container Materials for Nuclear Fuel Recovery Processes** by Paul D. Miller, Charles L. Peterson, Earl L. White, and Walter E. Clark

The selection of suitable materials for processing equipment is most important in fuel recovery. The problem arises because of the aggressive nature of the reagents that must be used to dissolve some of the spent fuel elements. In this investigation, corrosion tests were made under conditions simulating those that may occur in several proposed processes, in order that candidate materials of construction could be evaluated.

No material has been found which would allow both the hydrochlorination and dissolution steps of the vapor-phase Zircex process to be carried out in a single vessel unless corrosion rates of the order of 3 mils per month, or higher, could be tolerated. Several materials such as Inconel, Haynes 25, Type S-816 alloy, Illium R and the Hastelloys B and C appear promising for construction of a hydrochlorinator in a two-vessel process where the dry residue would be transferred to another vessel of, perhaps, titanium or tantalum for dissolution.

A variety of laboratory studies have shown that titanium will apparently withstand any condition likely to occur in the critical areas of the Darex process, including the dissolver and chloride-stripping column. It will undergo a severe attack in HCl vapor, but this is easily prevented by the presence of a small amount of nitric acid vapor or oxides of nitrogen.

**Evaluation of Materials of Construction for the Uranyl Ammonium Phosphate Uranium Recovery Process** by F. H. Meyer

A new uranium scrap recovery processing technique required the selection of materials of construction for the process. Many of the problems were solved by using lined equipment (rubber and Saran). The present paper deals with the evaluation of various metals in the phases of the process by means of an experimental in-plant test rack program in cooperation with the American Iron and Steel Institute and International Nickel Company.

## Inorganic Protective Coatings

**Chromium as a Protective Coating** by E. J. Seyb

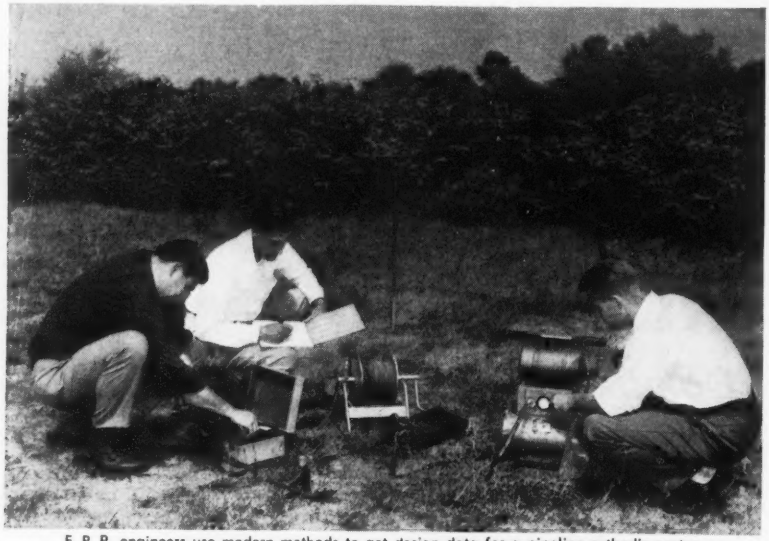
Although chromium is a relatively active metal, it passivates on exposure to air to give an exceptionally corrosion resistant coating. This resistance to oxidation is active at room and elevated temperatures. Because of the extreme inertness of chromium to oxidation, it is cathodic with respect to basic metals in most galvanic cells. Thus the primary protective value of chromium coatings is dependent on a continuous coating and to a lesser extent on low solubility of chromium corrosion products. These considerations have led to extended efforts in the past several years to improve corrosion resistance of plated articles by improving chromium deposits. Several approaches in this direction are described along with an estimation of the degree of practical success achieved.

**Precious Metal Plating and Corrosion** by Harold F. Smith

A partial summary of the methods of deposition of a group of precious metals including rhodium, platinum, silver and gold, along with the corrosion protection afforded by each is presented. Findings with respect to adhesion and corrosion or oxidation at elevated temperatures up to 2000 F are exhibited.

The use of nickel as an intermediate coating

(Continued on Page 81)



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# NORTH CENTRAL REGION ABSTRACTS

(Continued From Page 80)

between the base metal and the precious metal film is evaluated.

Finally, results of ball burnishing of the common precious metal deposits when subjected to high humidity and also salt spray tests is discussed.

**Electrodeposited Alloy Coatings** by Charles L. Faust

In corrosion the principal villain at moderate temperatures is moisture, at high temperatures, oxygen or other reactive gas. Alloy coatings can protect another metal from these corrodants better than single metal coatings. The alloys do so because of more favorable galvanic relationship to the basic metal, greater impermeability, better coverage and better resistance of the coating.

Better protection is not simply a matter of choosing the right alloy for its own chemical stability. The condition of the surface and the method of applying the coating can be critically important. The tendency for a coating to form a diffusion alloy with the basic metal needs consideration and is especially important for protection at temperatures above about 800 F.

Alloy coatings are applied by electrolytically codepositing two or more metals simultaneously and by electrodepositing layers of individual metals subsequently alloyed by diffusion. Alloy coating also is achieved by chemical reduction.

Frequently a choice must be made as to method of alloy plating. Each method will have special advantages and certain limitations. As for any process, each of the methods gives its best product only when the correct procedure is followed. Deviation causes inferior properties in a coating and incorrect preparation of the surface can defeat an otherwise good performance by a coating. Diffusion alloying with the basic metal can be a blessing or a detriment, which depending on the system involved.

The principal factors in attaining good protection are pointed out and illustrated by examples.

**Flame Plating** by J. F. Pelton

Flame Plating is a novel process for applying dense, adherent coatings of high melting metals, metal carbides, oxides and other materials. The process utilizes a detonation in a mixture of oxygen and acetylene to heat particles of the coating material, to surround them in a protective atmosphere and to propel them onto the workpiece at very high velocity. The part can be cooled during coating so that there is no warpage or metallurgical change in the base metal. There are some limitations on size and shape of parts that can be coated. Because of the high noise level, the coating operations are carried out by remote control in a soundproof cubicle.

A variety of coatings has been developed to meet differing needs of industry. Some of these are intended primarily for wear resistance at moderate temperature, while others are for corrosive environments or high temperature service in oxidizing atmospheres. Limited work has been done on coatings designed to protect other materials from high temperature oxidation.

Colored slides illustrate the basic process, production equipment and typical coated parts.

**Ceramic Coatings vs Metal Corrosion** by W. J. Plankenhorn

Porcelain enamels have been proved by long

(Continued on Page 82)


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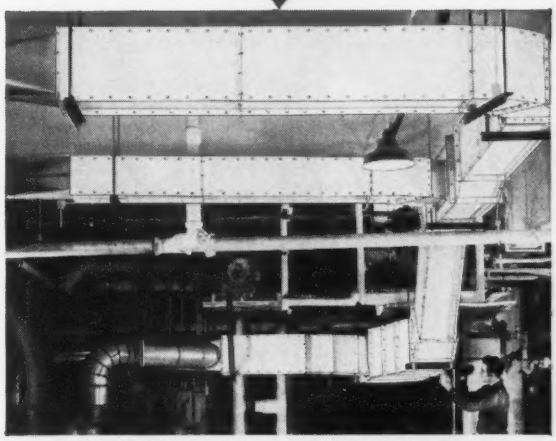

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# NORTH CENTRAL REGION ABSTRACTS

(Continued From Page 81)

years of experience to afford protection for metals against oxidation and corrosion under adverse conditions at temperatures approaching a red heat. Ceramic coatings, which may contain porcelain enamel frits fortified with refractory materials or be of the straight oxide type, have been effective in protecting metals and alloys at much higher temperatures.

Wide variations in the properties and characteristics of both porcelain enamels and ceramic coatings can be produced through the selection of the frit and the mill added materials and also by controlled differences in processing. It has not been possible to develop a single universal coating with a high degree of all the desirable properties. Consequently, it is generally necessary to develop a porcelain enamel or a ceramic coating for each specific application of which there is an ever increasing number.

## Corrosion Problems in the Utilities Industries

**Soil Oxidation Reduction Potential Determination** by Roger E. McVey

Anaerobic corrosion of iron in soil occurs as the result of the activity of sulfate-reducing bacteria. The degree of soil reductiveness, which can be measured as the oxidation-reduction potential, serves as an index of the severity of anaerobic corrosion.

A method of determining areas conducive to this type of corrosion involves the use of the newly developed soil redox probe for measuring this oxidation-reduction potential.

The field use of this probe, including probe cleaning procedures and calibration are presented.

**Plastic Coated Pipe** by H. M. McDaniel

A brief history of sales and experiences with plastic pipe is given as a background for the early work on plastic coated steel pipe. The development of the present day coating is traced step by step based on several combinations of coatings which were produced and tested. Various means of evaluating coatings are described. Slides are used to illustrate the process of applying a continuously extruded plastic coating over steel pipe.

**Use of Filming Amine for Prevention of Corrosion in Condensate Systems** by Edward E. Galloway

The use of filming amine to protect turbines and condensate systems against carbon dioxide and oxygen corrossion is covered. Filming amine has been used for almost two years at 1250 psi and 900 F in a central power station where carbon dioxide and oxygen are normally quite high. Effects on corrosion test specimens in various locations before and after the use of filming amine are presented. Other data pertaining to the effects of the filming amine on turbine erosion-corrosion also are presented.

**Glass Fiber Reinforcing of Coatings** by B. A. Graham

Glass compositions, chemical and physical properties of glass fibers are presented. Reinforcing properties for corrosion resistant coal tar coatings are compared to reinforcements for plastics. In describing the forms of glass fiber used, comparisons are made between monofilaments and multiple strands and reinforcing properties vs fiber diameter and comparison of glass fiber mats and woven fabrics. Types of binder and size used on the fibers are discussed in relation to compatibility with coal tar coatings and the temperatures encountered in hot coating application.

Benefits to corrosion protection are cited from laboratory tests and field results. Impact resistance demonstrated.

Future improvements in glass fiber reinforcing are predicted, including use of more fiber, new forms of fiber and application in thin film coatings.

## Organic Protective Coatings

**Structural Design and Corrosion** by C. G. Munger

The purpose of the paper is to demonstrate the points or areas in modern construction which are most subject to corrosion and which are most difficult to protect. This is demonstrated by laboratory experiments showing that edges, corners, wedges, rivets and similar common structural configurations are focal points for corrosion and therefore need extra protection. Each of these focal points is described, including a suggested method for solving the problem.

**A Classification of Protective Coatings According to Their Performance** by Kenneth Tator

Various protective coating types in successful current industrial use are analyzed. In presenting this analysis, the various coating types are classified according to their basic fundamental resistances and preferred uses. Material costs and application costs also are considered in making this classification.

**Practical Aspects of Protective Coating Specifications** by J. R. Allen and G. Mackey

Points requiring careful consideration prior to the actual preparation of practical and adequate protective coating specifications are discussed. These include exposure conditions, type and condition of substrate, size and shape of items to be coated, economics, local limitations, shop or field applications and color requirements. With this background, the development of specifications for surface preparation, coating system, application and inspection is reviewed. In addition, the follow-up required to insure that the specifications are met in both shop and field applications is outlined.

**Acid Brick and Corrosion Resistant Mortars in Chemical Construction and Maintenance** by Thomas E. Roñay

Concrete and steel have only limited usefulness and life as materials of construction in chemical environments. The protection of these two and similar most commonly used materials of general construction can be achieved by a wide variety of methods ranging from the application of a protective coating of a few mils thickness, to the application of a brick lining cemented in place with suitably chosen, chemically resistant thermosetting mortars. In many instances, this latter method of maximum protection is clearly indicated and has found wide application in food, beverage, textile, steel and chemical industries. Certain pre-design and construction criteria are of great importance for the success of the subsequent application of brickwork. These special criteria hold equally true for the construction of acid-proof vessels, as well as acid-proof floors.

To insure maximum service life of both the base construction materials and the acid-proof brickwork, the use of a membrane between the two is necessary.

The choice of the most suitable acid brick and corrosion resistant mortar system will generaly depend on the nature of the corrosive atmosphere, the process method and temperature. Design and construction of the base structure and the acid-proof brickwork as well as criteria for the proper selection and testing of the membrane and mortar materials is discussed from the point of view of the design plant and maintenance engineer, as well as the contractor and applicator.

## Developments in Corrosion Resistant Metals

**Some Recent Developments in Light Metals** by Paul D. Frost

Aluminum is the brightest star on the light metals horizon at the present time. Although the supply of all light metals exceeds the demand, aluminum has been less adversely affected than magnesium and titanium by the recession that started in mid 1957 because of the large commercial market enjoyed by the aluminum industry. In contrast, the cut-backs and stretch-outs in military projects have drastically reduced outlets for magnesium and titanium products.

The biggest consumer of aluminum continues to be the building industry. The comparative inertness of aluminum to weather, the light construction possible and the increasing use of colorful, anodized surfaces makes aluminum a most attractive construction material for residences, office structures, plants and bridges.

The automotive industry is using more aluminum each year in passenger cars, mostly in automatic transmissions and body trim. The 1958 usage averages about 45 pounds per car (Chrysler products use about 100 pounds per car). This is expected to increase each year and reach an average of about 80 pounds per car by 1965.

A major development that may drastically increase this consumption is the very recent interest in hyper-eutectic aluminum-silicon alloys (up to about 25 per cent silicon) for engine pistons and possibly engine blocks. High-silicon alloys have been used in the past in Germany because of their low thermal expansion coefficients. If these alloys prove satisfactory in engine parts for automobiles, this application could become the largest single consumer of aluminum.

In aircraft and missile fields the introduction of the new X2020-T6 aluminum alloy promises to extend the usefulness of aluminum into the 300-400 F range. This alloy contains about one per cent lithium and has lower density, a higher elastic modulus and higher elevated temperature strength than the strongest of current aluminum alloys.

While total military consumption of magnesium and titanium are down, interest in these metals for specific applications is high. With attention being focussed on missiles and satellites light-weight alloys of magnesium are extremely important. Magnesium-lithium alloys are included in this interest because of their very low densities.

Titanium is finding an ever-increasing market in chemical plant and marine construction where its superb corrosion resistance makes it superior to other metals in many applications. The new all-beta B120-VCA titanium alloy holds considerable promise in applications requiring good strength and formability.

**Uncommon Engineering Metals** by L. F. Kendall, Jr. and J. P. Denny

This discussion brings engineers and designers up to date on some uncommon metals. The following information is discussed for zirconium, hafnium, vanadium, columbium, tantalum, chromium and rhenium: Availability, cost, physical and mechanical properties, fabrication and applications.

**New Developments in Heat Treatment Improve Corrosion Resistant Alloys** by Walter A. Luce

The complex high alloy stainless materials require careful handling during production and fabrication to assure maximum corrosion resistance. Improper thermal treatments may produce physical changes in the alloy, other than common chromium carbide formation, which markedly reduce its resistance to sulfuric acid and other similar corrosives. Data are presented on work done to study the formation, effects and prevention of this phase in cast and wrought compositions of the high alloy stainless type. Reference to the deleterious effect of secondary phases in other complex high alloys is made also.

**Developments in High-Strength, Corrosion-Resistant Alloys** by F. H. Beck

After a review of developments at other laboratories, a new precipitation hardening cast stainless steel is described. Some corrosion and mechanical properties of the alloy in both the solution annealed and aged conditions are presented. Metallographic studies show the alloy, 25% Cr, 5 Ni, 3 Cu, 2 Mo and 0.04 max C, to be a duplex structure (austenite-ferrite). The age hardening is believed to result from sigma phase in finely divided form.

**Recent Developments in Oxidation Resistance and Protection of Refractory Metals** by C. T. Sims

Relative oxidation behavior and degree to which oxide properties affect the oxidation resistance of columbium, tantalum, molybdenum, tungsten and rhenium are presented. Recent work in development of oxidation-resistant columbium and tantalum alloys is reviewed and the current status of protection of molybdenum by cladding and coating discussed.

# NORTH CENTRAL REGION BIOGRAPHIES

**J. R. ALLEN**—Senior Service Engineer, Engineering Service Division, Engineering Dept., E. I. du Pont de Nemours & Co., Inc. He does consultant and development work on protective coatings and thermal insulation. He has a BS in ceramic engineering, Georgia Institute of Technology. After army service he joined duPont in 1946 and spent eight years on research and development of non-metallic materials for chemical equipment, two years in insulation and design work, then assumed his present position.

**FRANKLIN H. BECK**—Associate professor and assistant director of the Corrosion Research Laboratories at the Ohio State University, Engineering Experiment Station. After receiving his BS in metallurgical engineering from the Pennsylvania State University in 1943, he was employed by the E. I. du Pont de Nemours and Company. He later entered the graduate school of the Ohio State University where he earned his PhD in 1949. Dr. Beck is the author and co-author of a number of corrosion articles.

**RUDOLPH A. BENDER, JR.**—Since May, 1958, with Bender & Assoc., he has had a long career of activity in the brewing field starting in 1934 as chemist and bacteriologist for Cataract Brewing Co., Rochester and subsequently in various capacities with Hialeah Brewing Co., Belmont Brewing Co., White Rose Brewing Co., Time Brewing Co., A. Gusmer, Inc., The Pfaudler Co. He has a BChE in physical chemistry from Marquette University and Master Brewer Fermentology, Wahl Henius Institute. He is author of numerous technical papers in his field and is a lecturer on brewing industry problems. He is a member of seven technical organizations.

(Continued on Page 83)

# NORTH CENTRAL REGION BIOGRAPHIES

(Continued From Page 82)

**WALTER K. BOYD**—A project leader of the Corrosion Research Division, Battelle Memorial Institute, holds a degree in metallurgical engineering from The Ohio State University and has specialized in metallurgical aspects of corrosion since 1945.

Mr. Boyd has considerable experience in the development of special alloys. He has contributed to development of both low- and high-temperature corrosion-resistant stainless steel alloys and lately has been active in the development of corrosion-resistant uranium and zirconium materials. He is an active member of the National Association of Corrosion Engineers.

**D. M. CARR**—Vice-president of engineering for The Chemical and Industrial Corporation, since 1950 he has made seven trips to Europe and visited many states of the union in connection with construction and operation of ammonium nitrate plants. He has a BS in chemical engineering, University of Washington, 1925 and for 25 years worked for E. I. du Pont de Nemours & Co., on numerous plants in various capacities, including plant manager.

**JOHN P. DENNY**—Physical Metallurgy Specialist, General Engineering Laboratory, General Electric Co., Schenectady, N. Y. After service in the Army Air Corps he became research engineer at Battelle Memorial Institute, leaving there in 1947. His present work with General Electric includes precipitation hardening, high temperature alloys, cermets, bearing materials. He has a BS metallurgy, Colorado School of Mines, 1942; MS metallurgy, University of Utah, 1948; PhD metallurgy, University of Utah, 1950. He is a member of ASM and AIMME.

**O. B. ELLIS**—Senior Research Engineer, Armo Steel Corp., has a BS in chemistry, 1922 and an MS in physics, 1924 from University of Louisville, Ky. He has been in the company's research laboratories since 1932 where he supervises corrosion research.

**SYLVAN B. FALCK**—Since 1951 vice-president, Inner-Tank Lining Corp., Cincinnati. He formerly was employed as chief control chemist, Pharmaceutical Div., Bristol Laboratories, Syracuse; E. I. du Pont de Nemours & Co., U. S. Food and Drug Administration and the War Production Board. He has a BS in chemistry, Johns Hopkins University.

**CHARLES L. FAUST**—Chief of the Electrochemical Engineering Div., Battelle Memorial Institute, Columbus, Ohio. He is a past president of The Electrochemical Society, formerly a member of its board, is active in editing and preparing for publication books and periodicals relating to plating and is author or co-author of more than 60 technical articles, chapters in five books and has over 40 patents. His division is concerned with various aspects of metal finishing, electrolysis, batteries and waste disposal. He has a PhD in chemical engineering, 1934, University of Minnesota, was on the War Metallurgy Committee and now is consultant for the Materials Advisory Board of the National Academy of Science. He belongs to four technical organizations.

**FREDERICK W. FINK**—Battelle Memorial Institute, is chairman of the Corrosion Principles symposium for the NACE 15th Annual Conference and 1959 Corrosion Show to be held March 16-20, 1959 in Chicago. Mr. Fink joined NACE in 1947 and has served in various capacities. He was head of arrangements for the educational lectures for the NACE 14th Annual Conference held in San Francisco, March 1958. He is a past chairman of Technical Committee T-3 on General Corrosion Problems and presently is serving on the ISCC Subcommittee on relations with Foreign Technical Organizations.

He has been with Battelle Memorial Institute since 1938, joining the staff as a corrosion engineer. Last year he was made chief of the corrosison research division at the institute.

**MARS G. FONTANA**—A past-president of NACE, he is professor of metallurgical engineering and research at Ohio State University. He holds several degrees, has received many honors including the NACE Speller Award and is author and co-author of numerous papers on corrosion processes. He also acts as consultant on corrosion problems for several big industrial firms.

**WAYNE Z. FRIEND**—In charge of the Corrosion Engineering Section, Development and Research Division, The International Nickel Co., Inc., New York. He has been with the division

(Continued on Page 84)

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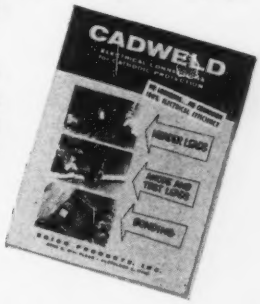


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(Continued From Page 83)

since 1937. He is a BSChE from West Virginia University (1924) and MSChE (1926) from the same school. Before 1937 he was associated with Gasoline Recovery Corp., Charleston, W. Va., and with Philgas Div., Phillips Petroleum Co. Boston and Detroit.

**PAUL D. FROST**—Chief, Light Metals Division, Battelle Memorial Institute, received a B of Metallurgical Engineering degree from Rensselaer Polytechnic Institute in 1940 and has taken graduate courses at The Ohio State University. He was a metallurgical engineer with the Republic Steel Corporation, 1940-1943; taught metallurgy for Cornell University Extension School, 1943-1945; and was with the Cornell Aeronautical Laboratory, 1943-1945. At Battelle since 1946, Mr. Frost has had extensive experience in the physical metallurgy of aluminum, magnesium and titanium alloys and in hot and cold working of these metals.

**EDWARD E. GALLOWAY**—The author graduated from Ohio State University with a BChE degree in June, 1949. He has been employed as a staff engineer since July, 1949 with the Cincinnati Gas & Electric Company.

**B. A. GRAHAM**—He is with L-O-F Glass Fibers Co., Waterville, Ohio and has been active in development, evaluation and production of glass fiber materials for ten years. With a BS in chemical engineering, University of Michigan, 1940, he spent part of his army service with Manhattan Engineering District. His other industrial experience includes five years in the paint, plastics and rubber fields. He is a member of the Society of Plastics Engineers.

**A. E. HOWE**—He has a BS in Engineering, Massachusetts State College, 1920. Mr. Howe has had a wide experience in industry, including job electroplating as owner of the Tumble Barrel Plating Company, several years with NRA and Non-Ferrous Foundry Code Authority and three years with Cladite Inc., in charge of the Development Laboratory for Metallic Pigmented Paint. He spent six years in research, development, promotion and consulting on electropolishing and finishing with Lucius Pitkin, Inc. and five years with Federal Telephone and Radio Corporation as Supervisor of the Finish Engineering Department. Mr. Howe joined General Electric in Bloomfield in 1948 as an engineer in finishes and corrosion and joined the General Engineering Laboratory in 1956 as Engineer-Finishes and Corrosion. Fields of specialization are: Atmospheric and natural water corrosion; Electropolishing, electromachining techniques, and electroplating; Protective and decorative coatings for metals.

**ALFRED D. JENSS**—District manager, Cincinnati office, Ampco Metal, Inc., he has held several positions with his present employer and for 10 years was with the Harnischfeger Corp. He is an alumnus of University of Wisconsin.

**STANLEY KASS**—He has been with Westinghouse Electric Corporation since 1946, having transferred to the Bettis Atomic Power Division in 1952 where he now serves as Lead Engineer, Corrosion Section, Nuclear Core Department. He received a BS in Chemistry from Ohio University in 1943. Mr. Kass' principal field of work is in the corrosion behavior of nuclear reactor materials including zirconium, uranium, hafnium and their alloys.

**W. J. KRETSCHMER**—Senior Corrosion Engineer, Gas Engineering Dept., Columbia Gas System Service Corp., Columbus, Ohio. Almost all of his time since 1939 with the Service company has been occupied with corrosion control of pipelines, cables and other utility property. He attended the electrical engineering department of Ohio State University College of Engineering, is a member of several NACE technical committees, of the AGA corrosion committee and past chairman of the AGA subcommittee on underground corrosion.

**LOUIS P. KENDALL, JR.**—Presently Nuclear Materials Engineer, General Engineering Laboratory, General Electric Co., he has an AB, chemistry, Princeton, 1941. He has been with du Pont de Nemours & Co. as analytical chemist and supervisor, worked on the Manhattan District project at Oak Ridge and Hanford and has been with General Electric since 1946. He belongs to ASM and ACS.

**IRVING S. LEVINSON**—Sales manager, Technical Products, Ampco Metal Inc., he is a graduate of the University of Michigan and the University of Illinois in metallurgy. He has been employed also in oil refineries, in gasoline plant construction, and as chief metallurgist, Celanese Corp., Chemistry Division.

**WALTER A. LUCE**—A graduate of the Ohio State University in 1943 with a bachelor of chemical engineering degree. He worked as a process engineer for the Curtis-Wright Corporation specializing in materials problems and following duty with the U. S. Navy obtained his MS in metallurgy from Ohio State in 1947. Since that time he has been associated with The Duriron Company, Inc., handling sales and development problems in metallurgy and corrosion.

**GUERARD MACKEY**—Now a specialist engineer in the Design Division, E. I. du Pont de Nemours & Co., Inc., where he is responsible for protective coating specifications on new construction. He joined duPont in 1930 and has worked on many aspects of maintenance, cleaning, machine development and maintenance painting. He has a BS in mechanical engineering, University of Illinois, 1930.

**H. M. McDANIEL**—Since 1953 he has been with the Pipe Sales Division, Republic Steel Corp. working on sales and development of plastic pipe and plastic coated steel pipe. He formerly was employed at Oak Ridge, Tenn. by Tennessee Eastman Corp. and later by the same company in plastic sales at Kingsport, Tennessee. He has a BS in chemical engineering, University of Tennessee, 1942.

**ROGER E. McVEY**—A member of the Engineering Department of the Pittsburgh Group, Columbia Gas System. He has been in the underground corrosion field since 1955. Received a BS in biological science from Marshall College, Huntington, West Virginia, in 1951. He is a lieutenant in the USNR and a member of NACE.

**W. D. MANLY**—Metallurgist at Oak Ridge National Laboratories, where he does research on high temperature materials used in atomic energy work. He has a BS and MS in metallurgy from University of Notre Dame. He belongs to several engineering organizations including NACE and is a frequent contributor of technical material on his engineering specialty. He is active on NACE technical committees.

**F. H. MEYER**—Associate Research Physicist, Continental Oil Co., Ponca City, Okla. A member of the American Physical Society, the American Crystallographic Association and the American Chemical Society, he has a science degree from the College of the City of New York and an MS in physics from Polytechnic Institute of Brooklyn.

**PAUL D. MILLER**—Has been with Battelle Memorial Institute for the past 20 years working on physical chemistry problems. His interests include aqueous molten salt and gas-phase reactions with a variety of metals. He recently has been closely associated with a project directed toward establishing the role of ferrous hydroxide in corrosion reactions, particularly with reference to steam power station operation.

He also has done work on flue-glas corrosion and directed considerable attention to successful protective treatments by publication of papers. He holds several patents.

He has a BS from Manchester College and MA and PhD degrees from Ohio State University in physical chemistry.

**C. G. MUNGER**—Vice-president in charge of manufacturing and research for Amercoat Corp. He has been active in NACE for many years both as an officer and on technical committees. Since 1936 his principal work has been in connection with corrossion research, particularly on steel and on concrete exposed to sewage conditions. He has worked on numerous problems for the armed services, the Atomic Energy Commission and private industry especially in connection with application of coatings and plastics.

He frequertly speaks before technical organizations and has written numerous papers in his field. He has a BA in chemistry, Claremont College and did work in graduate chemistry there. Besides NACE he belongs to numerous other technical organizations.

**J. F. PELTON**—He now heads coating development work at the Speedway, Indiana laboratory of Linde Company as assistant manager of development. He has a BS in chemical engineering, University of Tennessee and MS in the same field from Carnegie Institute of Technology, 1940. He worked for Linde Company at its Tonawanda, N. Y. laboratories on growth and fabrication of synthetic crystals.

**J. H. PHILLIPS**—Senior Technical Advisor, National Aluminate Corp., Chicago since 1956. He directs technical aspects of contract research. From 1947 to 1955 he was chief chemist for Babcock and Wilcox Co. and section head of the Chemical Research Section at its Alliance, Ohio research center. He also was employed by Mallinckrodt Chemical Works, St. Louis where he worked on the Manhattan District project. He has AB and BS degrees in chemistry from Southwest Missouri State College and did graduate work in chemistry at University of Chicago. He is a member of ACS and ASTM.

**WILLIAM J. PLANKENHORN**—Assistant director of research for Chicago Vitreous Corp., a division of The Eagle-Picher Co. He worked as a ceramic engineer for several midwest manufacturers after graduation from University of Illinois in 1931 with a BS in ceramic engineering. He also was employed by Borg-Warner and obtained an MS in ceramic engineering from University of Illinois in 1949.

His research work at University of Illinois concerned work sponsored by various groups at the Wright Air Development Center and included ceramic coatings on metal components of aircraft power plants. He published several papers in this field. He started work for his present employer in 1954. He is a member of American Ceramic Society.

**THOMAS E. RONAY**—Supervisor of laminated products development for The Richardson Co., Melrose Park, Ill. He formerly was vice-president in charge of research and development for Nukem Products Corp. A native of Hungary, he attended University of Heidelberg and has BA and MA degrees in physical chemistry from University of Buffalo. Among five technical organizations he is a member of NACE.

**FREDERICK S. SCHULTZ**—Supervisor in the Rocket Engine Section, Malta Test Station, General Electric Co., Ballston Spa, N. Y. He has an AB in chemistry, Kansas State, Pittsburg, Kan., and PhD in physical organic chemistry, Iowa State College, 1950. He worked for five years as pigment chemist for Eagle Picher Lead Co., Galena, Kans. and later for Airosol, Inc., Neodesha, Kans. He worked first for General Electric as an insulation engineer, and in 1953 was appointed supervisor of Finishes Engineering for the Aircraft Gas Turbine Division, Evendale, Ohio.

**EDGAR J. SEYB**—Research Supervisor, Detroit Laboratories, Metal and Thermit Corp. Since 1950, when he joined United Chromium, Inc., since absorbed by Metal and Thermit, he has worked on deposition of chromium and related metals. He has been co-author of papers in his field. He has a BA, Sterling College, 1946 and PhD University of Kansas, 1950. He is a member of ACS, ECS and AES.

**CHESTER T. SIMS**—Assistant chief, Nonferrous Physical Metallurgy Division, Battelle Memorial Institute, Columbus, Ohio. His experience includes 2½ years research on corrosion and inorganic chemistry problems and 6 years in nonferrous physical metallurgy. In the latter field he has been concerned mainly with investigations of molybdenum, columbium, tantalum, tungsten, cobalt and particularly with rhenium. He has a BSci, Northeastern University, Boston and a BSci in chemical engineering. He also has an MS in metallurgical engineering, Ohio State University.

**W. J. SINGLEY**—Senior engineer, Westinghouse Electric Corporation, Bettis Atomic Power Division, Pittsburgh. Prior to joining Westinghouse, he spent five years at Mellon Institute, on an International Nickel Company Fellowship. He is currently employed in the Bettis Boiler Development Group investigating methods of preventing chloride stress corrosion attack of austenitic stainless steel tubed steam generators. He has a BS in chemical engineering, Lehigh University, 1949.

**HAROLD F. SMITH**—President, Smith Electrochemical Co. Cincinnati, which specializes in unusual plating processes and allied chemical operations. Before founding his present company, he worked for a number of years in electroplating, developing and manufacturing dry plate rectifiers and in other electrochemical work. He has a degree in chemical engineering and has done graduate work at University of Cincinnati. He is a member of AES, National Association of Metal Finishers and the Engineering Society of Cincinnati.

**KENNETH TATOR**—Head of Kenneth Tator Associates, Coraopolis, Pa. which specializes in corrosion and abrasion prevention. He has a BA in chemistry, 1928, Reed College; and MS, chemical engineering, 1930, MIT. He worked with natural and synthetic resins for Dewey & Almy Chemical Co., Cambridge, Mass., for the War Production Board and as a chemical consultant with the Bureau of Industrial Conservation. He organized and operated the firm of Industrial Lining Engineers, Pittsburgh, 1944-1949. He is a member of numerous technical organizations, including NACE, has published many papers in his field and is a frequent speaker on coatings technology.

**A. A. WATTS**—Supervisor of Materials Research, Rocket Engine Section, Aerojet-General Corp., Sacramento, Cal. In his present capacity he has worked for two years on materials prob-

(Continued on Page 85)

## NATIONAL and REGIONAL MEETINGS and SHORT COURSES

**1958**

Oct. 5-8—Northeast Region. Somerset Hotel, Boston, Mass.

Oct. 15-17—North Central Region. Cincinnati, Ohio.

Oct. 20-24—South Central Region. New Orleans, Roosevelt Hotel.

Nov. 17-19—Western Region. Los Angeles, Statler Hotel.

**1959**

Jan. 12-14—Canadian Region. Montreal, Quebec.

Feb. 11-13—Canadian Region. Calgary, Alberta.

March 17-19—15th Annual Conference and 1959 Corrosion Show. Sherman Hotel, Chicago.

Oct. 5-7—Northeast Region. Lord Baltimore Hotel, Baltimore, Md.

Oct. 12-15—South Central Region Meeting, Denver, Col.

Oct. 20-22—North Central Region, Cleveland.

**1960**

March—16th Annual Conference and 1960 Corrosion Show. Dallas, Texas, Memorial Auditorium.

No dates set—South Central Region Conference, Tulsa, Okla.

Oct. 11-14—Northeast Region Meeting. Huntington, W. Va.

**1961**

March—17th Annual Conference and 1961 Corrosion Show. Buffalo, N. Y., Hotel Statler.

Oct. 24-27—South Central Region Conference, Houston, Shamrock Hotel.

**1962**

March—18th Annual Conference and 1962 Corrosion Show. Kansas City, Municipal Auditorium.

October 16-19—South Central Region Conference, San Antonio, Texas.

### SHORT COURSES

**1958**

Nov. 10-14. Corrosion Short Course. Key Biscayne Hotel, Miami. Miami and Jacksonville Sections, NACE.

Nov. 20-21—Los Angeles Section. Corrosion of Underground Structures.

**1959**

June—Teche Section. Corrosion Control Short Course.

## Teche Section Meeting

Scheduled for the July 31 Teche Section meeting, was a talk by Jack Stanton, Visco Products Co., Houston on "Guide to Corrosion Control in Oil and Gas Wells." Meeting place was the Petroleum Club of Lafayette, La. and the time was 6:30 pm.

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More than 20,000 cards have been issued by the NACE Abstract Punch Card Service.

## Miami Corrosion Control Short Course Is Nov. 10-14

A corrosion short course to be conducted November 10-14 at the Key Biscayne Hotel, Miami, was the main subject of a Miami Section meeting July 18. Committees for the short course were formed. J. B. Prime, Jr. of Florida Power & Light Co. was named director. The short course to be a joint enterprise of Miami and Jacksonville Sections.

The following persons have accepted invitations to participate in the course: T. P. May, The International Nickel Co.; Raymond Hadley, Sun Pipe Line Co.; J. W. Pedlow, Quelcor, Inc.; F. C. Weber, Phelan-Faust Paint Manufacturing Co.; A. G. Sternberg, Steelcote Manufacturing Co.

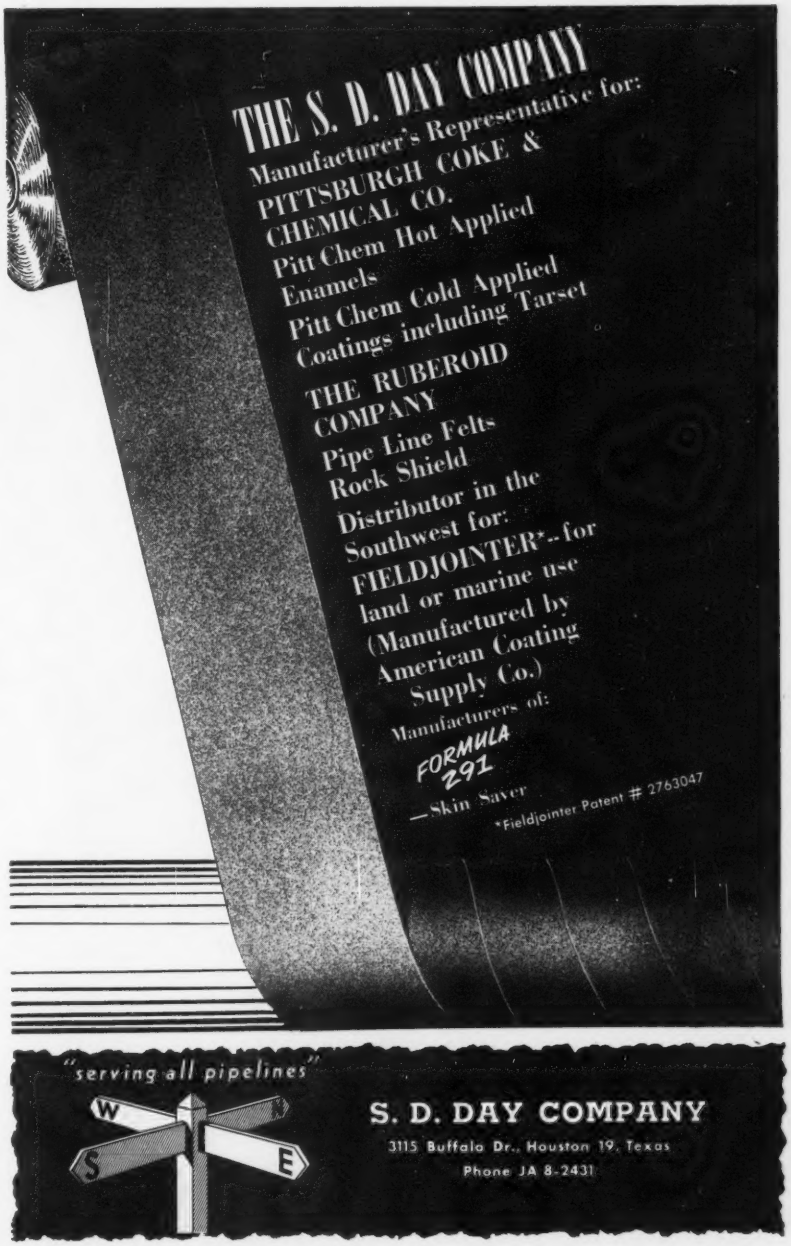
Also: A. H. Henning, The General Tire and Rubber Company; M. C. Miller, Ebasco Services, Inc.; W. J. Schwerdtfeger, National Bureau of Standards; Christopher Georges, Pipe Line Service Corp. and W. H. Howard, Shell Chemical Corp.

At the July 9 meeting of the section, a movie on aluminum finishes was presented. H. B. Bonebrake, Alcoa, was the speaker.

## North Central Biographies

(Continued From Page 84)

lems related to rocket propulsion, including corrosion research. His previous experience included cathodic protection work with Sohio Pipe Line Co., corrosion consulting and research work with C. F. Braun & Co., and physical and metallurgical research on titanium and other metals at Battelle Institute. After service in World War II as a bomber pilot, he gained a bachelor's degree in chemical engineering, Ohio State University and master's and PhD degrees in physical metallurgy. He specialized in corrosion work during his graduate studies.



# 12 Papers Are Arranged for Richmond Meeting

**SOME OF THE MEN responsible for the Western Region Conference and Corrosion Short Course to be presented November 17-21 in Los Angeles are shown here working on plans for the meeting. Seated at the table, left to right, John Brown, education chairman; Eric Bladholm, region chairman and John Richardson, program chairman. The group photo shows a meeting of the conference committee. From left to right, John Brown, Vincent Barnato, publicity chairman; Eric Bladholm, H. E. Tillman, facilities chairman; Ed Tandy, regional director; John Richardson, program chairman; William D. Roper, hospitality chairman and Frank Wilby, registration chairman.**

## *Southeast Region Sets Plant Trips, Ladies' Program*

Twelve technical papers will be presented in three sessions during the October 5-7 meeting of Southeast Region, National Association of Corrosion Engineers at Hotel Jefferson, Richmond, Va. Also planned are plant trips, a general business meeting of the region and a program for ladies.

Regional officers will meet beginning at 4 pm October 5 and a regional banquet held on the night of October 6.

The technical program is:

**Monday, October 6**

**Morning**

Chairman: Fred M. Reinhart, National Bureau of Standards.

Metallic Cations and Solid Metals as Corrosion Activators and Inhibitors in Acid Solutions, by Henry Leidheiser, Jr., Virginia Institute for Scientific Research and W. Roger Buck, III.

Stress Corrosion Cracking of Stainless Steels by John F. Eckel, Virginia Polytechnic Institute.

Study of Corrosion with the Aid of Large Single Crystals by Allen T. Gwathmey, University of Virginia.

**Afternoon**

Chairman: Armin H. Gropp, University of Florida.

Recent Developments in Corrosion Experimental Methods by Howard T. Francis, Armour Research Institute.

Recent Development at the International Nickel Test Station by T. P. May, The International Nickel Co., Inc.

Recent Developments in Corrosion Inhibitors by Harry C. Gatos, Massachusetts Institute of Technology.

**Tuesday, October 7**

**Morning**

Combating Tanker Corrosion, speaker to be named.

Marine Corrosion, Joseph B. Prime, Florida Power and Light Co.

Experience With Aluminum Pipe at Lake Maracaibo by R. S. Dalrymple, Reynolds Metals Co.

How to Save Dollars in Water Treatment, James H. Barnett, Corrosioneering, Inc.

Plant trips are to be held during the afternoon.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- Colors
- Painting Economics

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**MEMBERSHIP CARDS NEEDED AT CHICAGO**

**NACE members who are not pre-registered will be required to establish their membership in the association at the 15th Annual Conference in Chicago by showing their membership cards.**

**Registration fee for members is $10; for non-members, $15; for ladies $10.**

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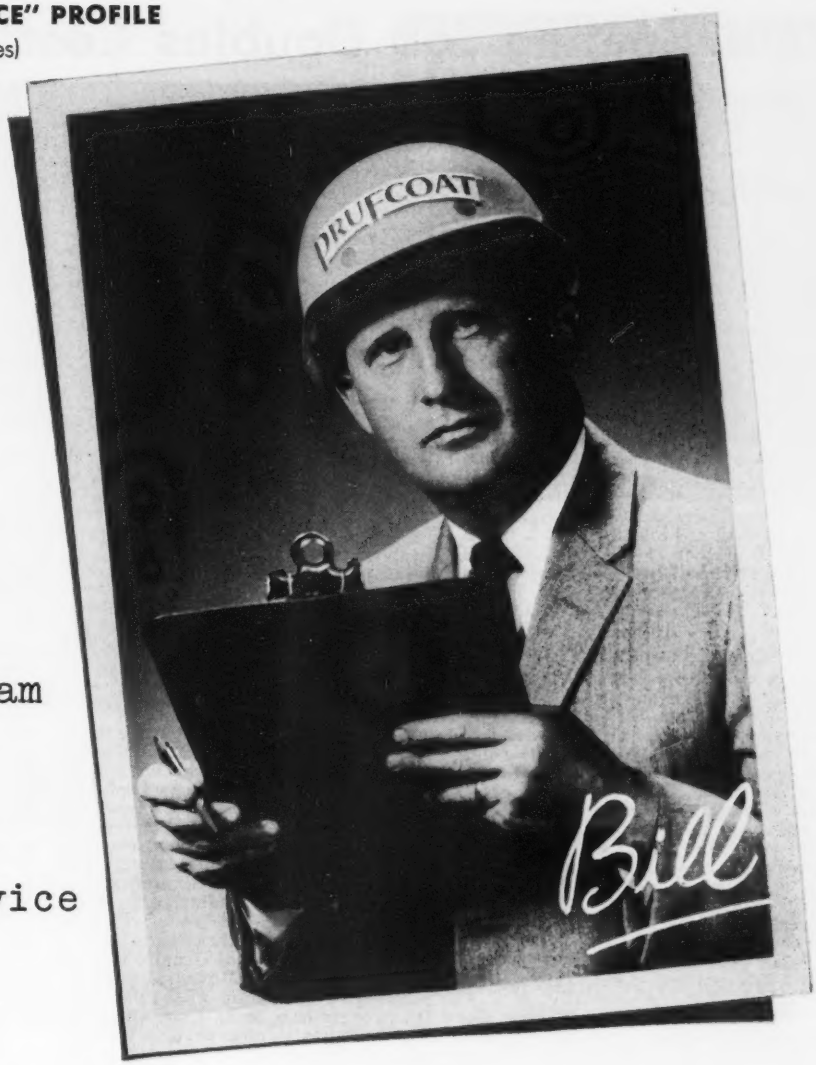


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*Your* Prufcoat representative can help you plan and execute the kind of corrosion-control program that will save you many precious new construction and maintenance dollars . . . and many maintenance headaches, too! There is no cost or obligation. Just write or call ● ● ●

**PRUFCOAT LABORATORIES, INC., 63 MAIN ST., CAMBRIDGE 42, MASS.**

# Poor Coating Job Doubles Cost in Five Years

## *Economics of Guarding Offshore Structures Discussed*

A poor coating system will increase the cost of protecting an offshore oilwell drilling platform by half during five years. This estimate was made by Robert M. Robinson, Senior Production Engineer for the CATC Marine Region of Continental Oil Company before a meeting of 119 members and guests of Houston Section. The dinner meeting was held August 12 at the newly remodeled Houston Engineering and Scientific Society headquarters.

Mr. Robinson discussed most phases of the problem of protecting both stationary and mobile drilling structures in the Gulf of Mexico. Corrosion control on a structure, he said, costs between 6 and 7 percent of the installed cost. Since a self-contained drilling platform may cost $900,000 in place, the importance of the corrosion control factor is obvious.

### Cost of Operations Cited

Among the cost estimates made by Mr. Robinson was one of $7500 to $8000 a day for operation of a rig and tender and associated equipment in 120 feet of water. He illustrated his talk with color photographs showing many of the points covered. These included an estimate of coating cost experienced by his company. Organic coating systems initially cost 40 to 55 cents a square foot; metallic systems 40 to 50 cents a square foot and tape more than 75 cents a square foot.

Of the systems used so far for protection of metal surfaces, he said, coatings are the best. New systems are under test on rigs, using Tator specimens.

Mr. Robinson cited as a principal aim the necessity to get complete coverage of surfaces. Incomplete coverage is no protection at all, he said. CATC practice is to seek designs which permit compete coverage, a principal means of accomplishing this being use of tubular members with as large diameter as possible. He also cited the necessity of scanning steel for "handles" welded on at fabrication plant, which result in coating hazards.

**HOUSTON SECTION members are shown here during the illustrated discussion by Robert M. Robinson, Continental Oil Co. on corrosion mitigation of offshore drilling structures. The August 12 dinner meeting was attended by 119 members and guests, the largest number in recent months.**

### Continuous Inspection Needed

Because a coating crew working on an offshore structure may cost $1100 a day with boat and $800 a day without, he said continuous inspection is important to secure the best possible performance and reduce lost time to a minimum. A good coating system, including touch-up, should cost about 15 cents a square foot per year over 5 years, he estimated.

The high cost of maintaining protection in the splash-tidal zone was indicated by some of the figures given. The square foot cost of Gunnite systems was given as $4.20; Monel, $4 to $6.50; petroleum base coating, glass reinforced, $6; wrought iron, $6.50. Epoxy-glass reinforced tape is now being tested, he said. Various means of fastening Monel sheathing are being used, including strap banding, drilling and tapping and stud guns. Patching of Monel is done by welding and a test of epoxy cement to hold patches is being tried now.

### Cathodic Protection Systems

Various schemes are used for cathodic protection of underwater steel, usually installed bare. These include 150-lb. anodes on galvanized cable giving 7-10 ma sq. ft. and a life of 2 to 2½ years. A test is to be made burying anodes in mud at base of structures to gain added anode life, he said.

Cost of Cathodic protection is about 4 to 8 cents a square foot a year with magnesium anodes. There is no appreciable difference in current drain between a well before and after wells are completed, he said.

All small size components are galvanized before installation. Usually galvanized coatings last about 18 months because high pH mud is used. Rusted components are replaced.

### Pipe Lines Protected

Gathering lines are coated with coal tar, glass, felt, kraft paper and cement coatings. Cathodic protection is applied at one end and tested at the other to insure its adequacy. Tank bottoms also are cathodically protected, and some have sumps through which water collected on bottoms can be drawn off.

Hulls of tenders are coated topside with alkyds and on bottoms with bituminous coatings.

Sodium nitrate and inhibited calcium chloride are used in the annulus of completed wells for corrosion protection. Bare tubing is used but no attempt is made to inhibit wells until salt water volume reaches 25 percent or some other indication is given inhibition is needed. Squeeze or tubing displacement methods are preferred for placing the inhibitor, although other methods have been used.

In gas wells tubes are coated with phenolic with an epoxy overlay. Use of aluminum grating is being considered for producing wells, but is not considered suitable for drilling structures because of the high pH of drilling mud.

Among other comments by Mr. Robinson in response to questions from the floor:

High zinc content coatings are being tried on welds.

(Continued on Page 90)

APEX for cathodic protection

MAGNESIUM ANODES

Corrosion control for under-ground and under-water pipelines and other metal structures regardless of all other methods used.

*Anode folders or technical consultation with our engineers available upon request.*

APEX Anodes are now available in 5 lb., 10 lb., 17 lb. and 32 lb. sizes. You may order bare anode with or without wire, or complete packaged anode with wire and back-fill ready for installation.

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Contractor states:
*"Best coating job I've ever done, only 5 holidays on total job."*

Pipe Line Superintendent says:
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## *On Multiple Line Laying*

An outstanding example on a multiple line laying job . . . consisting of two 6-inch and one 3-inch lines in *one* ditch . . . was recently completed in the Gulf Coast area. This entire multiple line laying operation was accomplished in gumbo soil.

POLYKEN . . . proven polyethylene tape was used on the entire project. The outerwrap that was used in this operation was Cathodic Protection Service's Dulux No. 2.

A single taping machine . . . a Betzel Tapemaster, a power driven, cleaning and taping machine . . . simultaneously cleaned, taped and outerwrapped all pipe, of both dimensions, before the lines were laid in the ditch. For further information regarding detailed applications, please call or write the CPS office nearest you.

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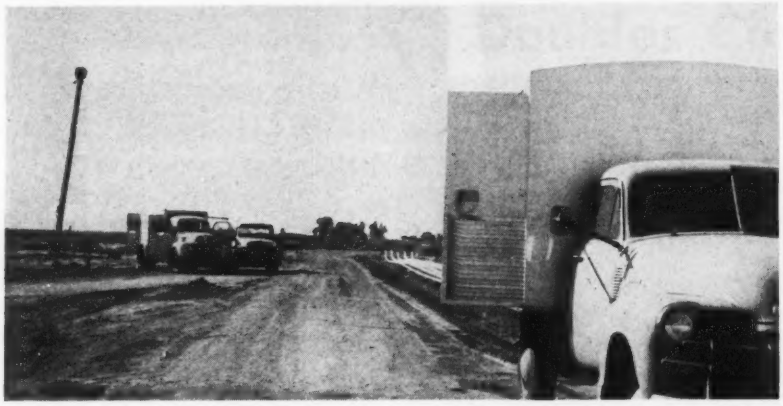

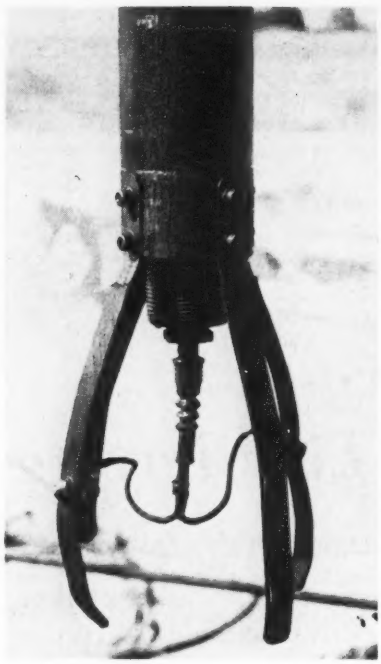

**This mobile equipment for cathodic portection subsurface testing will be seen on the San Joaquin Valley Corrosion Tour, Bakersfield, Cal., September 24-25. Top photo shows the rig on location testing for cathodic protection on an 11,192-foot well. The truck in the foreground contains a 120-volt, 100-ampere rectifier with infinite voltage adjustment. In the background are the hoist truck and submerged testing tool. At left is a closeup of the subsurface electrode.**

## Canadian Region Sets Double Meeting

Canadian Region is planning to hold two regional meetings instead of the usual one next year. A meeting will be held in the East in Montreal, Quebec, January 12-14, 1959 with Harrison Burbidge, Aluminum Company of Canada, Limited as chairman. A Western meeting will be held in Calgary, Alberta, February 11-13, with D. Stewart McIntosh, Britamoil Pipe Line Company, Limited as chairman.

Because of Canada's vast distances, meetings held in Eastern Canada have been poorly attended by NACE members living in the Western part of the nation and the reverse also has been true of meetings held in the Western section. B. H. Levelton, B. C. Research Council, University of B. C. is chairman of Canadian Region.

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South Central Region's 1961 Conference will be held October 24-27 at Houston's Shamrock Hotel.

## Everything Is Ready For San Joaquin Tour

Final arrangements have been made for the San Joaquin Valley Corrosion Tour, September 24-25. Registration headquarters will be set up in the lobby of the Bakersfield Inn, September 24 from 8 am to 11 am. Advance registration may be made by mailing the $15 registration fee to National Association of Corrosion Engineers, San Joaquin Valley Section, c/o Jack Penner, Magna Products, 305 E. Brundage Lane, Bakersfield, Cal. The fee includes bus fare for the tour for two days, one box lunch, the social hour and a luau dinner.

## Deep Ground Beds Is Topic at Birmingham

Maintenance and performance of deep sacrificial ground beds installed by the Mississippi Valley Gas Co. has been scheduled as the topic for the third quarter meeting of Birmingham Section, September 5. Ralph Hurst will be the speaker.

Members were requested to mail in or present at the meeting, questions on deep ground beds or other similar corrosion problems. Slides and motion pictures showing construction, maintenance and performance of deep ground beds the company has installed over a wide area of Mississippi were scheduled to be presented.

## Burnett Will Be Chairman Of Denver Region Meeting

Graydon E. Burnett, Bureau of Reclamation, Denver Federal Center, Denver, Colo. has been named general arrangements chairman for the October 12-15, 1959 conference of South Central Region at Denver.

## Technical Program For 1960 Northeast Meeting Outlined

A tentative technical program has been arranged and heads of principal committees selected for the October 11-14, 1960 Northeast Region meeting at Huntington, W. Va. R. G. Schroeder, Standard Ultramarine and Color Company, Huntington, general chairman, reported to regional trustees that five symposia and other details of the program have been arranged.

The symposia will be on protective coatings maintenance, inhibitors, fresh water corrosion, plastics, cathodic protection and chemical and refinery industry process corrosion. The usual meetings of technical and regional committees and social functions are being arranged in addition to plant tours.

Committeemen so far are: L. S. Van Delinder, Union Carbide Chemical Co., technical program chairman; William Tufts, Ashland Oil & Refining Co., local arrangements; George Cox, consultant, publicity and printing; R. Davisson, Union Carbide Chemical Co., publicity subcommitee; G. Trumbo, McJunkin Corp., printing subcommittee; Laban T. Moore, Tennessee Gas Transmission Co., registration; W. H. Williams, McJunkin Corp., finance; L. S. VanDelinder, technical committees.

## Kansas City Section to Chart Activities for 1959

A meeting to chart the activities for the coming year for the Kansas City Section will be held September 15. The meeting will be the first of the season. A film titled, Gas Goes To Market, furnished by the Gas Transmission Co. will be shown.

On November 10 Ralph Miller, Spencer Chemical Co. will talk on Corrosion in the Chemical Industry. Definite arrangements for the October meeting have not been made.

## Waldrip Speaks at Calgary

H. E. Waldrip, Gulf Oil Corp. was scheduled to speak at a meeting of Calgary Section September 21 on oil production corrosion problems. Mr. Waldrip is on a 6-week trip into Canada.

## Salleck to Run Course

John Salleck, Nocor Chemical Co. was named director for the Teche Section Annual Corrosion Short Course to be held in June, 1959.

## Poor Coating—

(Continued From Page 88)

Metco systems are being used in some cases.

Improper application is the principal reason for failure of coatings 95 percent of the time.

Management needs to realize the low bid is not always best on painting work. The price paid the contractor should be sufficient for him to make a profit while doing quality work.

Aluminum anodes have been used unsuccessfully.

Calcium chloride properly inhibited has been found less corrosive than sodium nitrate.

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# GRAPHITE ANODES ARE BEST!

## FOR LOW COST...

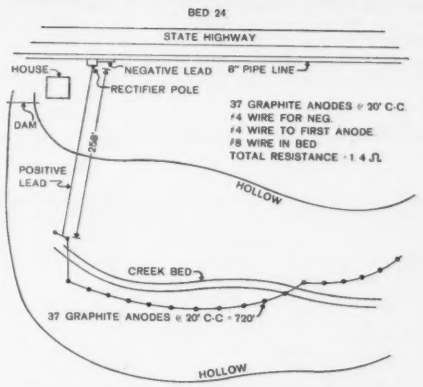
"National" graphite anodes provide good conductivity for economical ground bed design in both low and high resistance soils. Installed with graphite particle or coke backfill, "National" anodes offer low initial cost; exceptionally long life.

National Carbon manufactures a complete line of anodes providing the economies of graphite to all types of cathodic installations.

**3" x 60" and 4" x 80"**
**sizes in plain and NA Graphite**
**3" x 30" and 3" x 60"**
**NA Graphite Anodes with Type QA Connections**
**2" x 12", 2" x 20" and 3" x 30"**
**Type QA Anodes of NA Graphite**

**If you do not use "National" Graphite Anodes for cathodic protection, try them! We believe you'll find**
**"NATIONAL" GRAPHITE ANODES ARE BEST**
**FOR LONG LIFE AND LOW COST!**

## FOR LONG LIFE...




**50 "National" Graphite Anode Beds Protect 72 Miles of 8" Bare Pipeline**

In 1951, a corrosion control study was made of an 8" diameter bare pipeline in New York State. The line had been in service 15 years, and due to increased leaks, consideration was given to replacing it.

A corrosion survey performed by the Harco Corporation indicated cathodic protection could be provided with a rectifier type system to save the line. A total of 50 anode ground beds (utilizing 1500 "National" graphite anodes 3" dia. x 60" long in coke breeze backfill) and rectifier units were installed over a three year period, 13 beds in 1952...29 beds in 1953 . . . and the remaining 8 beds in 1954.

The pipe line is still in operation and there has been a significant decrease in leak frequency since cathodic protection was installed.

The terms "National" and "Union Carbide" are registered trade-marks of Union Carbide Corporation

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# Well-Balanced Boston Program Is Completed

## Several Regional Technical Committees Plan Meetings

Scheduling is complete, even to the assignment of times of presentation, for 40 technical papers to be delivered during nine symposia at the Northeast Region Conference, October 5-8 in Boston. Four technical committees also will meet.

Technical Committees T-5A-5 and T-2K will meet Monday, 1:00 pm.

Technical Committees T-3G and T-4F-1 will meet Tuesday, 1:00 pm.

Titles of papers, their authors and the symposia in which they will be presented are:

**Theory and Principles—10 am Monday**

Principles and Uses of Polarization Instruments by H. H. Uhlig, Massachusetts Institute of Technology.

Electrochemical Methods for Measurement of Corrosion Rates, by Milton Stern, Metals Research Laboratories Electro Metallurgical Co.

Studies on Oxygen Reduction Polarization Reactions by A. DeBethune, T. C. Licht, A. T. Pawlowski, D. C. Curran and A. J. Fekete, Boston College.

**Marine Corrosion—Monday, 1:30 pm**

Marine Corrosion Testing by T. P. May, International Nickel Co., Inc.

Lead—2 Per Cent Silver Alloy as an Inert Impressed Current Anode by K. N. Barnard, D. G. Gage and L. G. Christie, Naval Research Establishment, Halifax, Nova Scotia (read by J. H. Greenblatt).

Platinum Anodes for Cathodic Protection of Active Ships by H. S. Presier, Navy Bureau of Ships and B. H. Tytell, Boston Naval Shipyard.

Aluminum Anode Applications on Offshore Structures and Marine Pipe Lines by R. L. Horst, Aluminum Company of America.

The Effects of Velocity on Corrosion of Metals by H. R. Copson, The International Nickel Co. This paper will be presented to a combined session of the marine corrosion and the cathodic protection symposia.

**Cathodic Protection—Monday, 1:30 pm**

Designing Corrosion Control for Power Plants Using the Cathodic Protection Principle by L. P. Sudrabin, Consultant, Electro Rust-Proofing Corp.

Experiments with Zinc Anodes on Steel Piling by J. L. Kimberley, American Zinc Institute.

Current and Potential Relations for the Cathodic Protection of Steel in a High Resistivity Soil by W. J. Schwerdtfeger, National Bureau of Standards.

Electrode Reactions Associated with Galvanic Corrosion of Steel by H. E. Nelson, Socony Mobil Oil Co.

The Effects of Velocity on Corrosion of Metals by H. R. Copson, The International Nickel Co. Paper to be presented to a combined session of the marine corrosion and the cathodic protection symposia.

(Continued on Page 94)

### Registration Times; Schedule of Fees

**The following schedule will prevail:**

**Registration**

**Sun., Oct. 5—12 m-5 pm.**
**Mon., Oct. 6—8 am-5 pm.**
**Tues., Oct. 7—8 am-5 pm.**
**Wed., Oct. 8—8-10 am.**

**Desk located west lobby, Hotel Somerset, 400 Commonwealth Ave.**

**Fees: Including all meeting, industrial films, plant tours, cocktail hour—Members, $6; non-members, $8; lady guests, $3.50 (includes morning coffee).**

**Banquet Fee: Members, non-members, ladies, $6.50.**

**Clam Bake: Members, non-members, ladies, $6.**

## Naval Shipyard and Clapp Laboratories Tours Are Arranged

Tours have been arranged for Wednesday afternoon, October 8 to the Boston Naval Shipyard, Charlestown, Mass. and to Clapp Marine Laboratories, Duxbury, Mass. Transportation will leave from the hotel.

If there is sufficient interest to justify arrangements, tours also can be made to other plants, such as Monsanto Chemical, Everett, Mass.; General Electric, Lynn, Mass.; Sylvania and Raytheon plants in Greater Boston.

Tours to nearby Massachusetts Institute of Technology, Harvard, Wentworth, Boston University, Tufts, and other schools also are available.

### Marine Laboratories Scheduled for Tour

William F. Clapp Laboratories, Inc., a marine laboratory which makes no charge for its services is one of the tours scheduled during the Northeast Region Conference, October 6-8. The tour will be held October 8. Principal work of the laboratories is the study of the causes and prevention of deterioration of materials and structures by biological action and particularly by marine borers. Each month test panels from more than 300 locations throughout the world are received for study.

The laboratory makes no charge for its research and accepts only those projects which fall within the director's interest and resources. It is suported by voluntary contributions from individuals and organizations which benefit from its findings.

### Logan Joins Committee

Hugh L. Logan, National Bureau of Standards, Washington D. C. is a new member of the NACE Editorial Review Subcommittee. He will handle papers on stress corrosion.

## Important Northeast Region Committee Meetings Arranged

Important meetings of Northeast Region committees are scheduled during the October 5-8 sessions to be held at Boston's Hotel Somerset. Four of these meetings are open to all persons attending the conference while the regional board of trustees will hold a closed meeting.

The schedule follows:

**Sunday, October 5**

4 PM—Local Section and Meeting Attendance. E. A. Tice, Open Meeting.

5 PM—Corporate Membership. G. E. Best, Open Meeting.

**Monday, October 6**

4:45 PM—Regional Business Meeting. E. L. Simons, Open Meeting.

5:15 PM—Regional Board of Trustees Meeting. E. L. Simons, Closed Meeting.

**Tuesday, October 7**

5 PM—Local Section Program. A. F. Minor, Open Meeting. Program Chairmen of Local Sections.

### Variety of Entertainment Includes Ladies' Program

A variety of entertainment has been scheduled for the meeting. This includes a separate program of activity for lady guests. The arrangements committee also has listed a large number of interesting sights in and around Boston as well as some of the better known restaurants.

Entertainment features scheduled are:

Tuesday, Oct. 7—Cocktail hour, 5:45 pm. Banquet, 7 pm.

Wednesday, Oct. 8—New England Clambake, Plymouth, Mass., 5 pm, transportation arranged.

**Ladies' Program**

Monday, Oct. 6—10:30 am, registration, coffee. Open time for shopping, other activities.

Tuesday, Oct. 7—10:30 am, coffee, registration for fashion show and bus tours of historical landmarks with luncheon in one of Boston's historical eating spots. Cocktail hour, 5:45 pm. Banquet, 7 pm.

Wednesday, Oct. 8—10:30 am, coffee. Clambake, 5 pm.

Ladies who wish to do so may go on plant tours.

### Four Industrial Films To Be Shown Twice

Four industrial motion pictures will be shown on the afternoon of October 6 and repeated the following morning. The pictures are: "Corrosion in Action," The International Nickel Co., Inc.; "Zinc Controls Corrosion," American Zinc Institute; "Dimetcote—Life Time Protection for Steel," Amercoat Corp. and as "On the Line," Polyken Tape Div., The Kandall Co.

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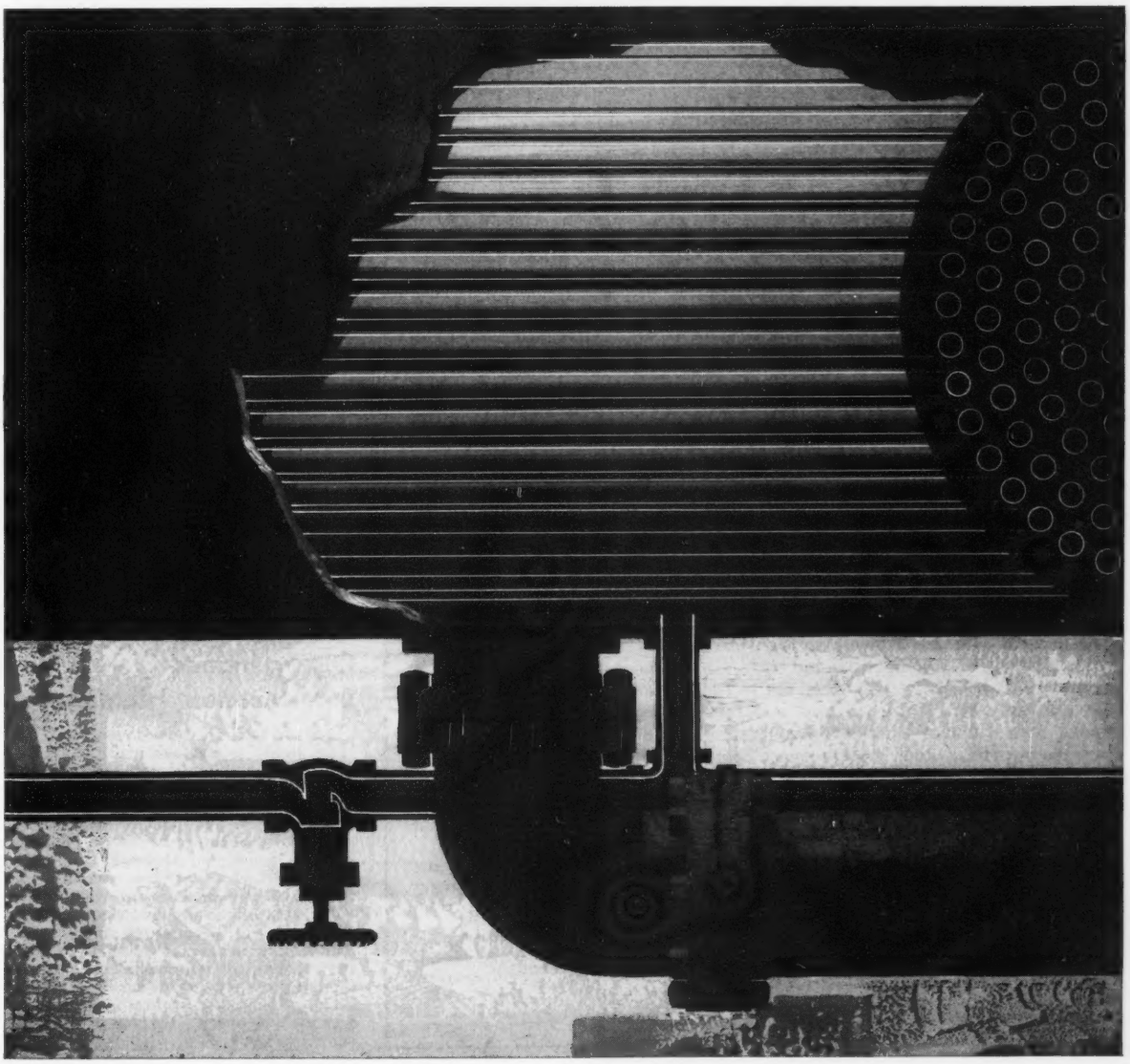


## Well Balanced–

(Continued From Page 92)

**Cathodic Protection—Tuesday, 9 am**

Application of High Silicon Iron anodes by W. A. Luce, The Duriron Co.

Performance of Zinc Anodes for Cathodic Protection in Sea Water by L. J. Waldron and M. H. Peterson, Naval Research Laboratory.

Graphite Anodes for Cathodic Protection by J. L. Miller, National Carbon Company.

Galvanic Anodes as a Supplement to Coatings in Brewery Pasteurizers by C. W. Ambler, Jr.

Cathodic Protection of Structures and Equipment in a Marine Environment by B. Douglas, Dow Chemical Co.

**Protective Coatings—Tuesday, 9 am**

Reactive Coatings by M. Kronstein, New York University.

Baked Phenolic Coatings for Use in Process Industries by L. S. VanDelinder, Union Carbide Chemicals Co.

Evaluation of Marine Service Coatings When Exposed to Tropical Environment by A. L. Alexander, B. W. Forgeson and C. R. Southwell, Naval Research Laboratory.

Reinforced-Plastic Coatings for Metals by W. R. Graner, Navy Bureau of Ships and Walter Park, Puget Sound Naval Shipyard.

A Modern Approach to Corrosion Resistant Coatings Through Epon Resins by W. C. Nauman, Shell Chemical Co.

**Marine Corrosion—Tuesday, 1:30 pm**

Uses and Abuses of Aluminum in Wooden-Hulled, Aluminum-Framed Minesweepers by T. H. Rogers and W. K. Chinn, Naval Research, Dockyard Laboratory, Halifax, Nova Scotia.

Design of Cathodic Protection Systems for Ships' Hulls by J. A. H. Carson Pacific Naval Laboratory, Esquimalt, British Columbia.

A Laboratory Evaluation of Zinc Anodes by J. A. H. Carson, Pacific Naval Laboratory, Esquimalt, British Columbia, W. L. M. Phillips and J. R. Wellington, Consolidated Mining and Smelting Company of Canada, Ltd.

Zinc in the Marine Environment by E. A. Anderson, New Jersey Zinc Co.

**Protective Coatings—Tuesday, 1:30 pm**

Coal Tar Coatings and Surface Preparation by W. F. Fair, Jr., The Koppers Co.

Chemically Modified Coal Tar Coatings by W. E. Kemp, Koppers Co.

Polyurethane Protective Coatings—Properties and Applications by E. R. Wells, Mobay Research Laboratory.

Pipe Line Coating Performance by H. W. Wahlquist, Ebasco Services, Inc.

The Corrosive Resistance of Glassed Steel by D. K. Priest, The Pfaudler Company.

**Utilities Industries and Special Applications—Wednesday, 9 am**

Liquid Metals for Use in a Nuclear Reactor by W. D. Manly, Oak Ridge National Laboratory.

The Effect of Minor Contaminants on the Corrosion Behavior of Ferrous Alloys in Liquid Sodium by E. G. Brush, General Electric Co.

Corrosion Problems Associated with Steam Generators and Condensers in the Nuclear Power Industry by L. R. Scharfstein, Westinghouse Electric Corp., Bettis Plant.

Instruments for Measurements in Corrosion Work by K. G. Compton, Bell Telephone Laboratories.

**General Corrosion—Wednesday, 9 am**

Visual Demonstration of Corrosion Processes by G. C. Cox, Consultant.

Glass Flake Reinforced Protective Coatings by A. Winsor Brown, Owens-Corning Fiberglas Corp.

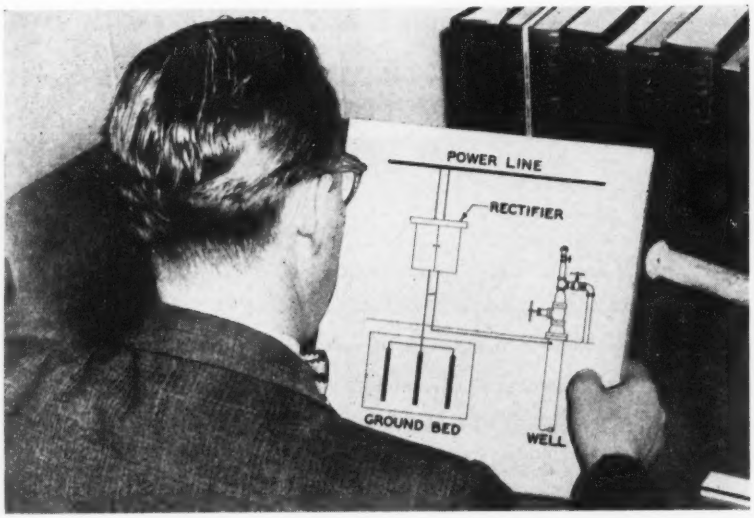
Some Effects of Stress and Composition on the Corrosion of Austenitic Stainless Steel by D. van Rooyen, Westinghouse Electric Corp., Research Laboratories.

Some Characteristics of Sodium Silicate as a Corrosion Inhibitor by S. Matsuda and H. H. Uhlig, Massachusetts Institute of Technology.

## Old Fashioned Clam Bake Entertainment Highlight

An old-fashioned New England clam bake, held October 8, on the waterfront in historic Plymouth will be the principal feature of entertainment at the Northeast Region Conference, October 6-8. After the clam bake, said to be a disappearing custom in the region, tours will be conducted through the replica of the vessel Mayflower and through the Clapp Marine Laboratories.

Because of the historic significance of the area, and because of fine vacation facilities, conference officials suggest that corrosion engineers bring their families to spend the entire week. Concerning the entire program, region trustees call it one of the finest ever presented in the region.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This major oil company has 33 of its wells in a pool in northwestern Kansas. Past experience indicated that external corrosion of casing would become a major maintenance item.

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# GENERAL NEWS

## Corrosion Course Is Offered at Houston U.

A full semester, 32-lecture evening corrosion course is offered for credit or audit by the University of Houston's College of Engineering. The course is titled CHE 460 and consists of two 1½ hour lectures weekly on Tuesday and Thursday evenings from 8 to 9:30.

Instructors for the course will be: Benjamin F. Davis, Jr., Aquaness Div., Hercules Powder Co., electrochemical theory; W. B. Brooks, Dow Chemical Company, metallurgy; H. E. Waldrip, Gulf Oil Corp., protective coatings, design, environment; Talmadge M. Heitman, Jr., United Gas Corp., cathodic protection. Each will give eight lectures.

Under electrochemistry such topics will be covered as corrosion in water containing oxygen, salt solutions, fully and partly immersed specimens, temperature, velocity, humidity. In the lectures on metallurgical aspects, corrosion peculiarities of carbon and stainless steels, cast iron, non-ferrous alloys, including aluminum and magnesium will be covered.

Protective coatings lectures, among other things will consider surface coatings, surface preparation, application, metallic and organic coatings, aqueous environments and design. Principles of cathodic protection, current courses, determination of requirements and special effects of cathodic protection will be covered also.

## Louisville Industries Are Charged With 82% of Air Pollution Load

Industries in Louisville, Kentucky's West End industrial complex were found to contribute 85 percent of the air pollutants measured during a survey of the city by the Robert A. Taft Sanitary Engineering Center, Cincinnati, in cooperation with the Jefferson County Air Pollution Control District, U. S. Public Health Service, and other state, national and local agencies. Of the remainder, 9 percent was traced to domestic sources and 6 percent to transportation.

Of the industrial pollutants recorded 78 percent were gaseous and 7 percent solids.

The survey revealed about 440 tons of pollutants were discharged daily into the air over the West End, not including nitrogen, hydrogen, oxygen, carbon dioxide and water vapor.

The data were collected in an intensive campaign involving sampling of air for solids, bacteria, gases and obnoxious odors, and including meteorological factors. Through the use of fluorescent tracers, principal avenues through which pollutants were distributed were charted.

Included in the study were results of air pollution on materials. Steel spring

(Continued on Page 96)

### Coatings School Set For September 6 and 13

**The practical coatings school to be given by Coatings Society of the Houston Area will have its first session September 6 and its second September 13. Those who miss the first Saturday can attend on the second Saturday, when the same schedule of events will be given. (See CORROSION, August, 1958, Page 95).**

**The school will be held beginning at 9 am each day at Hanna Construction Company, 9000 Airport Blvd., Houston.**

## Quick Identification by Crystal Facial Angles Is Facilitated by Catalog

Because the angles formed by the sides of a material crystals are always the same, it is possible to identify substances by measuring the angles of the crystal faces of an unknown substance and identify it by referring to a table in which the facial angles of crystals are listed with keys to the materials. Two recent developments have put this method of identification in the reach of nearly everyone: Publication of the Barker Index of Crystals (Volume 2 of the contemplated three volumes was published in 1957 and Volume 3 is scheduled to be published in 1958) and the invention of a small, relatively inexpensive goniometer with which crystal faces can be measured accurately.

The index to crystals, ultimately to cover 10,000 of the most commonly encountered materials, is based on the work of T. V. Barker of Oxford University, who devised a set of geometrical principles which would make it possible for any worker to select the same key classification angles on the surface of a crystal. His system was the outgrowth of a much more complicated system conceived by E. Frankenheim, a German crystallographer in 1842 and developed into a catalog of identifications by E. S. von Federov, a Russian, who compiled in 1912 an index of 10,000 materials which was published after his death in 1920.

By means of the catalog of crystal face angles it is possible to identify without chemical analysis as little as a single crystal of a material. An optical goniometer, developed by L. W. Codd makes measurement of the angles relatively simple.

## Papers on Environmental Testing, Simulation, Sought

Papers on environmental testing or simulation are sought for the April, 1959 annual meeting of the Institute of Environmental Engineers in Chicago. Raymond G. Yeager, Chrysler Corp., Missile Div., P. O. Box 2628, Detroit 31, Mich. is program chairman.

## ASTM Atmospheric Testing Results Given At Boston Meeting

Several matters involving corrosion control were considered during the June 22-27 meeting of the American Society for Testing Materials at Boston. Among the subjects were:

**Atmospheric Test Sites**—A summary of the final results of the program for determining the corrosiveness of various atmospheric test sites as measured by specimens of zinc and steel, was presented by Committee B-3 on Corrosion of Non-Ferrous Metals and Alloys. It was proposed that this study be expanded to include calibration of the test sites at Newark, N. J., Columbus, Ohio, East Chicago, Ill., and Freeport (Brazos River), Texas.

The 60 specimens each of 74 commercially produced non-ferrous metals and alloys are being placed at four test sites throughout the United States. The specimens have been analyzed for chemical composition, weighed and thickness measured. When withdrawn following exposure the specimens will be measured to determine loss in weight and depth of pits. The specimens will then be cut into tension specimens to determine loss of strength.

The second progress report on measurement of atmospheric factors of corrosion of metals was also presented. The data from this program are being analyzed to see if there is any correlation between the rate of corrosion and the factors of time-of-wetness, $SO_2$ concentration and temperature.

**Corrosion Resistant Steels**—Two subcommittees of Committee A-10 on Iron-Chromium, Iron-Chromium-Nickel and Related Alloys are working on the development of a specification for thin stainless steel sheets of 0.006 to 0.010 in. in thickness which are used primarily in aircraft. A test procedure will be established to accumulate data for specification limits.

Maximum carbon limits in low-carbon grades of stainless steel are being studied in detail. The object is to satisfy the producers from the standpoint of reasonable production procedures and to meet the demands of the chemical industry for corrosion resistance and the high-temperature interests for elevated temperature properties. This investigation will involve many ASTM groups as well as the ASME Boiler and Pressure Vessel Code, the American Welding Society, the Chemical Industry Advisory Board and the American Iron and Steel Institute.

Progress is being made toward ASTM specifications for high-temperature super strength alloys. Agreement has been reached that the alloys can be divided into four classifications: Iron-base, cobalt-base, nickel-base and stainless steel (precipitation hardening). There is good prospect of a specification by next year.

L. L. Wyman is chairman of the

(Continued on Page 98)

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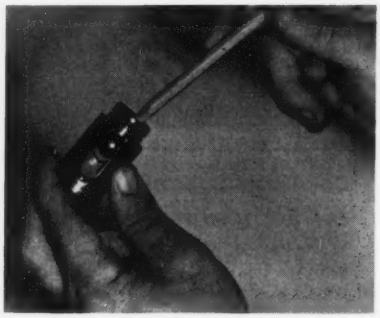

## Magnetic Ball Check Valve Uses No Springs

A magnetic ball check valve which does not require springs to close it and which can be made of corrosion-resistant materials can be used in many liquid systems. Designed to solve an oilwell corrosion problem by Harold Brown Co., Houston, the ball is readily moved from its seat by gas or liquid pressure. It returns to its seat automatically.

In gas lift wells, for example, the magnetic ball check valve fulfills several important requirements. Because it has no springs to corrode and break, failure from this cause is eliminated and the resultant backwash through an inoperative valve eliminated. This backwash may penetrate a casing and necessitate expensive repairs.

The ball is made of titanium carbide with a nickel binder. The cage is Monel into which magnets have been inserted. Magnetic force is sufficient to move the ball check to closed position where it is at a maximum, the position at which maximum force is needed. The force is weakest when the valve is in the opened position. The magnetic force has no influence on the process stream passing through it. It will open and close in any position.

The valve also is recommended for use in streams where contamination is an important factor or where the corrosion products of a valve spring would be harmful.

## Mathematics, Physical Sciences Course Offered

A new four-year curriculum in mathematics and the physical sciences, leading to a BS will be offered this fall by Stevens Institute of Technology, Hoboken, N. J. The curriculum will concentrate on basic theory and its general application in the several fields of physical science such as atomic physics, geophysics and physical chemistry.

Enrollment will not be limited to a specific number of students.

## ECS Meets September 28

Technical sessions on batteries, corrosion, electrodeposition, electronics (semiconductors), electro-organics, electrothermics and metallurgy and theoretical electrochemistry will be held at the September 28-October 2 meeting of The Electrochemical Society. The meeting will be held at Chateau Laurier, Ottawa.

## Metallurgists Are Sought

Metallurgists for work on catapults, arresting gear, aircraft and guided missiles are wanted by the Naval Air Material Center, Naval Base, Philadelphia 12, Pa. Pay scales range from $4490 to $8810 a year.

## Louisville Industries—

(Continued From Page 95)

test specimens were used to learn something about the varying rates of corrosion in the area. Springs mounted outdoors showed a loss of tensile strength greater than that of others when they were in the path of pollutants dispersed by prevailing southwest winds. It appeared the combined effects of outdoor exposure and air pollution were more destructive than the effect of air pollution alone.

To a limited extent it was discovered that the effect of exhaust gases from transportation vehicles was a factor in the pollution problem, but not to the same extent as in other cities.

Recommendations developed by the study include: Reduction of solid particle emission by burning fuel to less than 0.85 lb. per 1000 pounds of flue gas adjusted to 50 percent excess air for products of combustion. Maximum daily tonnage limitation on emission from any one plant. No emission of more than a ton a day of solids from any process operation. Reduction of irritant gases from fuel combustion. Reduction of untreated emission of odorous gases by at least 90 percent. Reduction of emission of hydrocarbon vapors.

Prohibit open burning of leaves and refuse. Coordination of activities in air pollution control with adjacent communities. A program of public information.

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Soil stress tests show the effective shielding action of J-M Asbestos Wraps. 18" coated sections of 4" O.D. pipe were buried in bentonite clay which was first wetted down and then allowed to dry out. At the end of 28 wetting-drying cycles, J-M Asbestos Wraps were found to give excellent protection to the enamel.

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The same research and field tests also demonstrated that J-M Asbestos Wraps provide the strong protection that strong coatings need and deserve. "Asbestos Wraps offer the most effective single protection against damage —prolong the working life of pipeline enamels." Here's why . . .

Asbestos is an ageless mineral. Fibers of asbestos are strong and tough . . . cannot rot or decay. As used in J-M Wraps, the fibers are felted, then impregnated with a coal tar or asphalt saturant to form literally a flexible covering of stone. These "stone-like" qualities form a durable shield—protect pipeline enamels from earth loads and soil movement which weaken coatings and permit pipe corrosion to set in.

Pipeline engineers are invited to write for their own copy of PP-34A, a *3-Point Study of Pipeline Coatings and Wrappers*, at no cost or obligation.

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## Corrosion Mechanisms Paper Presented by F. L. LaQue

Frank LaQue, International Nickel Co., Inc., New York, former president of NACE, and long prominent in its affairs, presented a paper, Corrosion Mechanics and Materials Selection Methods at the Golden Jubilee meeting of American Institute of Chemical Engineers, Philadelphia, June *22-27*.

A paper on Rubbers as Materials of Construction for the Chemical Process Industries by B. S. Garvey, Jr., Pennsalt Chemicals Corp., Wayne, Pa. said a basic reason for the use of rubbers is that they make possible better or cheaper equipment than that they make from other materials and have as good resistance to chemical attack.

The paper, Ceramic Materials for Corrosion Resistance in the Chemical Process Industries by Wayne A. Deringer, A. O. Smith, Corp., Milwaukee, Wis. emphasized the chemical qualities of ceramics as principal advantages in use of the material. Ceramics are used at temperatures too high or with corrosives too severe for metals to stand, he said.

•

Fifteen local corrosion control committees have affiliated with NACE's T-7 committee in two years.

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## ASTM Atmospheric—

(Continued From Page 95)

committee which will meet next in February, 1959, at the ASTM Committee Week, Pittsburgh, Pa.

**Zr, Cb, Mo, W, Li, U Studied**—Active task groups of Committee B-2 on Non-Ferrous Metals are working on tentative specifications for many of the uncommon or newer metals that are becoming important industrially such as zirconium, columbium, molybdenum, tungsten, lithium and uranium. Fact-finding groups are active on beryllium, tantalum, hafnium and thorium, but no plans for specifications have yet been set definitely. It is probable that a symposium on these uncommon metals will be held at the 3rd Pacific Area National Meeting, San Francisco, October 1959 to assist in gathering information for specifications.

The deleterious effect of arsenic in solder when used to join copper and brass products was discussed and steps are being taken to limit arsenic in solder to a safe level when used in this field of application. A symposium on solders and soldering is being planned for 1961.

Work is in progress on tentative specifications for titanium and titanium alloy welding rod and bare electrodes, as well as on titanium and titanium alloy bars and billet.

**Activated Carbon Vs Corrosive Gases**—The bad effect of organic vapors on contact performance can practically be eliminated by using activated carbon wafers in the sealed enclosure, according to James R. Laskie of National Carbon Co., speaking before Subcommittee IV of Committee B-4 on Metallic Materials for Electrical Heating, Electrical Resistance and Electrical Contacts. Good activated carbon adsorbs about half its weight in organic vapors. A minimum of 0.6 g activated carbon per 10 cu. in. of space is required.

The development of a method of bonding the carbon which makes it highly resistant to powdering from vibration while not reducing its ability to adsorb has made possible the fabrication of small compact pellets which may be fastened where desired with epoxy cement. In some cases baking operations for outgassing have been eliminated by using this getter.

E. L. Shobert is chairman of B-4 which will meet next in October in Chicago.

## St. Mary's Offers BS

St. Mary's University of Texas has added a four-year course leading to a bachelor of science degree, the first engineering degree to be offered by the school. The 164-hour course will blend humanistic and religious knowledge with scientific and technological growth of the student, according to school officials.

## Technical Illustrators' Organization Is Expanding

Technical Illustrators' Management Association is soliciting members nationally among persons interested in technical illustration problems. Those interested may get information from Keith Kinnaird, Technical Illustrators' Management Assoc., P. O. Box 1021, Hollywood 28, Cal.

*Now you can predict service life because Byers PVC Pipe Engineering brings a factual approach to piping system design*

# FACT:

## In sulfuric acid Byers PVC Pipe can out-perform stainless at 1/5 the cost

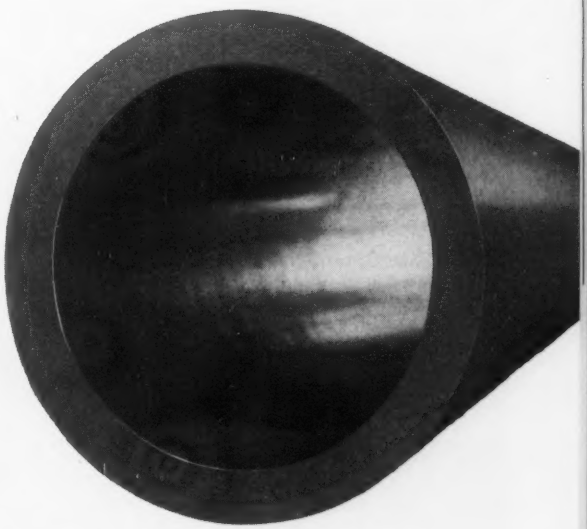
Stainless steel pipe often *fails* where Byers PVC Pipe *doesn't.*

Typical are sulfuric acid applications. Here, Byers PVC Pipe will not only out-perform stainless in terms of corrosion resistance — it also *costs less.* Only 1/5 the cost of stainless. That's why specification of Byers PVC Pipe makes such solid sense in this service.

The versatility of Byers PVC Pipe makes it ideal for many other corrosive services where metal pipe is either unsatisfactory or quite costly. Here are a few: acid fume vent piping, acid reactor blowoff lines, drain and sewer lines, and process lines handling acids, alkalies, oxidizing agents, alcohols, brines, plating solutions, slurries, and many other fluids.

Where product purity is important, Byers PVC Pipe is especially suitable. *It will not contaminate.*

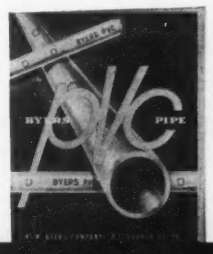
A talk with a trained Byers field service representative can cut your corrosion bills, save you money. No obligation, ever. A. M. Byers Company, Clark Building, Pittsburgh 22, Pennsylvania.



Byers PVC Pipe is available in sizes ¼" through 6", in schedules 40, 80 and 120.

Type I — compounded of pure PVC resin for normal impact and outstanding corrosion resistance.

TYPE II — compounded of pure PVC resin modified with plasticizer for high impact resistance in mechanically punishing applications.




Write our Engineering Service Department for copy of new 32-page illustrated catalog on Byers PVC Pipe.

**BYERS PVC PIPE**

# BOOK NEWS

**Cathodic Protection of Buried Structures.** 30 pages, 7¼ x 9¾ inches, paper. December, 1957. Joint Committee for Coordination of the Cathodic Protection of Buried Structures, Central Electricity Generating Board, 24-30 Holborn, London EC 1, England. Availability not indicated.

A general discussion of the theory of corrosion, especially as it applies to underground metal. The second chapter deals with applications of cathodic protection and the third considers interference problems.

Chapter four describes some of the information the committee is interested in getting concerning cathodic protection.

**Industrial Maintenance Painting.** Second Edition. By Paul E. Weaver. 189 pages, 5¼ x 8¼ inches, flexible cloth. 1958. Paul E. Weaver, 4025 Brady St., Baton Rouge 5, La. Per copy, $5.50.

This edition expands on the wide variety of information useful to industrial maintenance painters that appeared in the first edition. Prices have been brought up to date and new information developed since 1955 included.

Contents include surface preparation, coating characteristics, spray equipment, shop painting, inspection, specification writing, paint testing, comparative costs, design, cost estimating, tank cars and vessels, solvents, colors, painting economics, notes on coatings and cathodic protection. There is a bibliography, schedule of references, a glossary and an alphabetical subject index.

The book is written in an informal style in simple language and is suited to the needs of the painter who has not had formal coating education. A principal feature that should prove useful are the tables which give data not readily found elsewhere, and which are comprehensive in coverage of the whole maintenance coating problem. Examples are tabulated data giving approximate square feet per linear foot and per ton for different steel members and average surface area per ton of steel for different types of construction.

**CORRECTION**

**In August CORROSION, under the heading BOOK NEWS the following book was mentioned, but the price indicated was incorrect. Here is the title and the correct price:**

**Korrosionstabellen Metallischer Werkstoffe.**
**Fourth Edition. (In German) By Franz Ritter. 290 pages, 6½ x 9½ inches, cloh. 1958. Springer-Verlag in Wien I, Molkerbastei, Austria. Per copy, $11.65.**

**7th Biennial Corrosion Tour.** 27 pages, 8½ x 11, paper cover. 1958. Permian Basin Section, National Association of Corrosion Engineers, Availability not indicated.

This is the printed report of the Seventh Annual Corrosion Tour conducted by Permian Basin Section NACE. The tour covered a wide area and numerous exhibits in the vicinity of Midland, Odessa, Big Spring and other oil producing centers nearby.

Exhibits inspected are described and a consensus is given by observers concerning the condition of the exhibits and effectiveness of the corrosion control methods used. These exhibits included many which have been seen repeatedly during the course of the preceding tours. They include such structures as pilot water flood systems, cement and plastic lined gun barrels, stock tanks, flowlines coated in place, treaters, sucker rod strings, coils and others.

**Anti-Corrosion Mannual.** 260 pages, 8½ x 11, cloth. Corrosion Prevention and Control, 140 Cromwell Road, London, S.W. 7, England. Per Copy, 2 Pounds Sterling, 10 shillings not including postage.

The first edition of a proposed annual publication giving practical information on corrosion control. A considerable percentage of advertising is included in the book.

Contents include, introduction to corrosion and its prevention, fretting, cathodic protection, instrumentation, corrosion resistant materials, surface preparation techniques, organic and metallic coatings, wrapping and spray packaging. Many of the articles are adapted from articles in the periodical "Corrosion Prevention and Control" and others are written by persons prominent in British corrosion control work, or supplied by companies and trade associations.


# Corrosion Can Take a Holiday

**IN PIPE COATINGS AND WRAPPINGS OR IN PROTECTIVE PAINTS**

Tinker and Rasor Holiday Detectors can assure this fact. They are an insurance policy that you are getting what you pay for in applied protective coatings. Tinker and Rasor pipeline (jeeps) holiday detectors are your inspector's right hand. They can give him the best quality control possible. On transmission lines he can spot trouble, as soon as it develops, such as clogged sprays on dope machine (which leaves pipe uncoated but covered with outerwrap), carbonized particles in bitumens, etc.

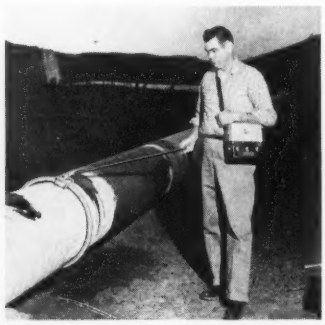
MODEL HP US Patent #2629002 (electrode)

LINE-TRAVELING

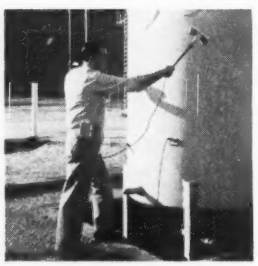
The model HP self-contained line-traveling detector, has its own power supply (wet cell battery); needs no ground wire and operates equally well on damp or dry pipe. Adaptable on any size transmission pipelines.

SHOULDER-PACK

Tinker and Rasor shoulder-pack holiday detector is designed to give the best possible inspection. It offers an adjustable voltage output range from 5,000 to 20,000 volts of sharp pulse type voltage which puts less stress on protective coatings. This equipment is available with conductive silicone brush type electrodes (non-fouling in soft coatings), for inspecting flat or irregular surfaces and with full and a half circle spring electrodes. This model will inspect damp or dry coating equally well and, as in all Tinker and Rasor detectors, has audible bell signal.



MODEL EP



MODEL M 1

PAINT AND THIN FILM

Tinker and Rasor Model M 1 detector is used for inspection of thin films where complete protection is a necessity. The detector has a bell alarm signal and is equipped with a leather case and belt loop. The potential of inspection is 67 volts. Not a spark detector, it operates with a damp cellulose sponge mounted on a phenolic wand handle. Pin holes can be pin pointed by using a corner of the sponge once a holiday has been detected.

**TINKER & RASOR**

417 Agostino Rd.(P.O. Box 281), SAN GABRIEL, CALIF. • ATlantic 7-7942

**DISTRIBUTORS:** Crutcher-Rolfs-Cummings, Inc., Houston, Texas, Remco Manufacturing Company, Inc., Tulsa, Oklahoma, Canadian Equipment Sales and Service, Ltd., Edmonton, Alberta, Bob Herrick, Rentals and Service, Harrisburg, Penna., Falcon Line Products Corp., Elizabeth, N.J.
Export Agents: Frazar and Hansen, Ltd., San Francisco, Calif.

# 200-hour torture test proves SCOTCHRAP superiority!

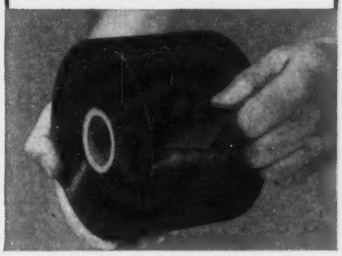
REG. U.S. PAT. OFF.
BRAND
PIPE PROTECTION TAPE

Each of these 5 standard pipe lengths was covered with a different commercial pipe "protective" coating—both tapes and mill-coatings. All five pipes were then put in the barrel shown with an abrasive-chip tumbling medium and continuously tumbled for 200 hours. This unretouched photo shows the results: only the pipe coating on the extreme right survived *intact*—the pipe wrapped in "SCOTCHRAP" Brand Pipe Protection Tape. This photo shows clearly and dramatically why "SCOTCHRAP" gives such superior performance in resisting abrasion from backfilling and underground soil stresses. Add to this the superior resistance to electrolytic forces . . . the superior shear adhesion strength . . . and the new low prices, and you have the reasons why we believe "SCOTCHRAP" Pipe Protection Tape is your best total coating buy for entire distribution systems.

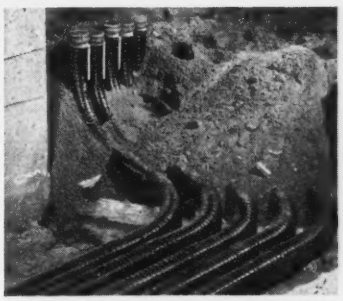
"SCOTCHRAP" is a registered trademark of 3M Co., St. Paul 6, Minn.

**"SCOTCHRAP" Pipe Protection Products**

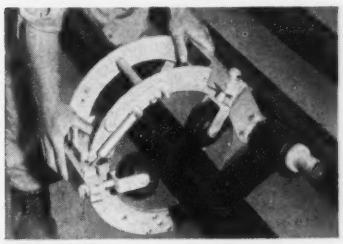
**LOOK what you can do with "SCOTCHRAP"**



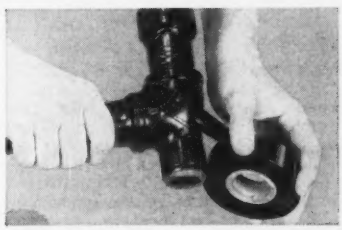
**MAKE QUICK,** easy applications to any size pipes. "SCOTCHRAP" is specially formulated polyvinylchloride in handy tape form. It is tough, but conformable; sticks at a touch . . . no heat . . . no mess!



**ACTUAL** field use shows why abrasion-resistance of "SCOTCHRAP" is important: backfill is coarse, rough—could easily puncture or tear less tough coatings.



**SAVE TIME** on total system coverage. With wide-width "SCOTCHRAP" and "Betzel" Tapester, one man covers 200 feet of 4″ pipe in less than 30 minutes.



**INSULATE** joints, tees, elbows in the field. Supercomformable "SCOTCHRAP" does it quickly. For complete information on "SCOTCHRAP", or to arrange demonstration, write: 3M Co., 900 Bush Ave., St. Paul 6, Minn., Dept. BQ-98

**MINNESOTA MINING AND MANUFACTURING COMPANY**
**. . . WHERE RESEARCH IS THE KEY TO TOMORROW**

3M COMPANY

# Equipment Services NEW PRODUCTS Materials Literature

## Air Pollution

**Catalytic Reduction** of nitrogen oxides to harmless free nitrogen is effected by a system installed at Koppers Co., Inc., Arroyo, W. Va. plant. Catalytic Combustion Corp., Detroit 8, Mich., built the system which handles nitric acid and nitrogen oxides produced at toxic levels from an acidulation process.

## Ceramics

**Ceramic** materials can be formed into extremely thin corrugated or other high surface area structures permitting for the first time fabrication of ceramic heat exchangers, catalyst supports and lightweight structural units. The techniques developed by Minnesota Mining & Mfg. Company's subsidiary American Lava Corp., Chattanooga, Tenn. permit forming ceramics such as magnesium aluminum silicate, zirconium oxide, bonded silicon carbide and others into complex shapes, much in the way metals are formed, but which are no longer ductile in final form. Applications for the shapes are seen in high temperature heat exchangers and other similar uses.

## Coatings—Organic

**Zirco,** a synergistic drier catalyst permits formulation of paints without lead. Developed by Advance Solvents and Chemicals, 500 Jersey Ave., New Brunswick, N. J., the material is said to activate on catalyze drying metals such as cobalt and manganese. A bulletin is available on the material.

•

**Dresser Red-"D",** a new shop coat will give over six months' protection against corrosion of pipe couplings, according to Dresser Manufacturing Division, Bradford, Pa. The coating can be cleaned with gasoline or carbon tetrachloride and is compatible with more than 95 percent of field coating systems used on pipelines today. It is non-toxic in potable water.

•

**Permatron Co.,** 2117 East York St., Philadelphia 25, Pa. produces a one-coat organic finish in brass, gold, copper, bronze and a variety of colors which can be sprayed, dipped or roller coated before baking between 400 F for seven minutes and 325 F for 15 minutes. Metals coated thus have the appearance of solid metals. The coating is suggested as substitute for plating and anodizing.

•

**Dag Colloidal Graphite** dispersions are being used to protect electric typewriter parts against corrosion and permanently lubricate them at the Elmira, N. Y. plant of Remington Rand Division of Sperry-Rand Corp.

•

**Powdered Vinyl Resins** available from Polymer Processes, Inc., 125 N. Fourth St., Reading, Pa. are being used to produce fused vinyl coatings on metal surfaces. The process involves heating metal parts to be coated above the flow temperature of the vinyl resin and then dipping the parts into a bed of dry fluidized vinyl powders which melt and encapsulate the object and bond by fusion to its surface. Uniform thickness from 10 to 50 mils are obtained in a single dip.

## Inhibitors

**PL-297,** a compound which coats copper-bearing surfaces and acts as a chemical insulator is seen by DuPont Company's petroleum Chemicals Divisions as useful in hydrocarbons where it is desirable to eliminate catalytic effects of copper or copper-bearing alloys, or to increase stability of gasolines in presence of copper.

•

**Hagan Phosphates** for boiler water conditioning are described in Bulletin HSP-906 available from Dept. 410, Hagan Chemicals & Controls, Inc., Box 1346, Pittsburgh 30, Pa.

•

**A Proportional Chemical Feeder,** designed for use in connection with cooling towers, evaporative condensers or air washers that has no moving parts has been developed by Water Service Laboratories, Inc., 615 West 131st. St., New York 27, N. Y. The feeder, attached to a chamber containing a solid, water-soluble chemical captures a small amount of water from the spray, permits it to circulate over the solid chemical where some is dissolved, and then to flow back into the system. The unit, which weighs from 15 to 25 pounds, has been tested for more than two years and found to operate successfully.

•

**Cooltex,** a transparent chemical coolant for grinding operations being marketed by the Texas Company, gives good rust protection even when highly diluted, according to W. E. Kuhn, general manager of Texaco's Research and Technical Department. It leaves no sticky film on surfaces.

## Instruments

**Liquid Probe,** an attachment for the D-K Analyzer, produced by Delsen Corp., 719 W. Broadway, Glendale 4, Cal. permits direct readings of dielectric constants and dissipation factors of most non-conductive liquids. It can be installed as a continuous monitor.

•

**Shandon Electropolishers** produce electropolished surfaces in 10 seconds under controlled conditions. Potentiostats made by the firm, designed to control electrode potentials to any desired value, have a range of applied potential between electrolyte and test piece from 0 to plus or minus 2 volts and output current variable from 0 to plus or minus 50 ma. More information is available from Shandon Scientific Company, Ltd., 6 Cromwell Place, London S. W. 7, England.

## Insulators

**Roseal,** a polyethylene butyl rubber resin with high resistance to corrosive fumes, greater resistance to moisture than other non-metallic sheaths and easier pulling because of its waxy construction has been patented by Rudolph A. Schatzel, vice-president of engineering of Rome Cable Corp. The cable sheathing compound has been tested both as a sheath and as insulation over a period of two years.

•

**Pesco** nylon insulating couplers were improved in 1956 to eliminate field starting problems. More data and a list of dealers are available from Plastic Engineering & Sales Corp., P. O. Box 1037, Fort Worth, Texas.

## Metals—Ferrous

**Allegheny Stainless** in Chemical Processing, a 40-page booklet is now available on request from Advertising Dept., Alleghen Ludlum Steel Corp., Oliver Bldg., Pittsburgh 22, Pa. A table of the corrosion resistances of all the company's stainless steels is included.

•

**4-D Wrought Iron,** A New Dimension in Corrosion Control, is available on request from A. M. Byers Co., P. O. Box 1076, Pittsburgh 30, Pa. Tabulated data are given on the comparative resistance to numerous typical corrosive conditions of the new 4-D, standard wrought iron, and alternate ferrous materials.

## Metals—Non-ferrous

**Carpenter Titanium** Tubing and Pipe, an 8-page illustrated brochure, describes products made of titanium by the firm's Alloy Tube Division. Diagrams are given of corrosion resistance.

•

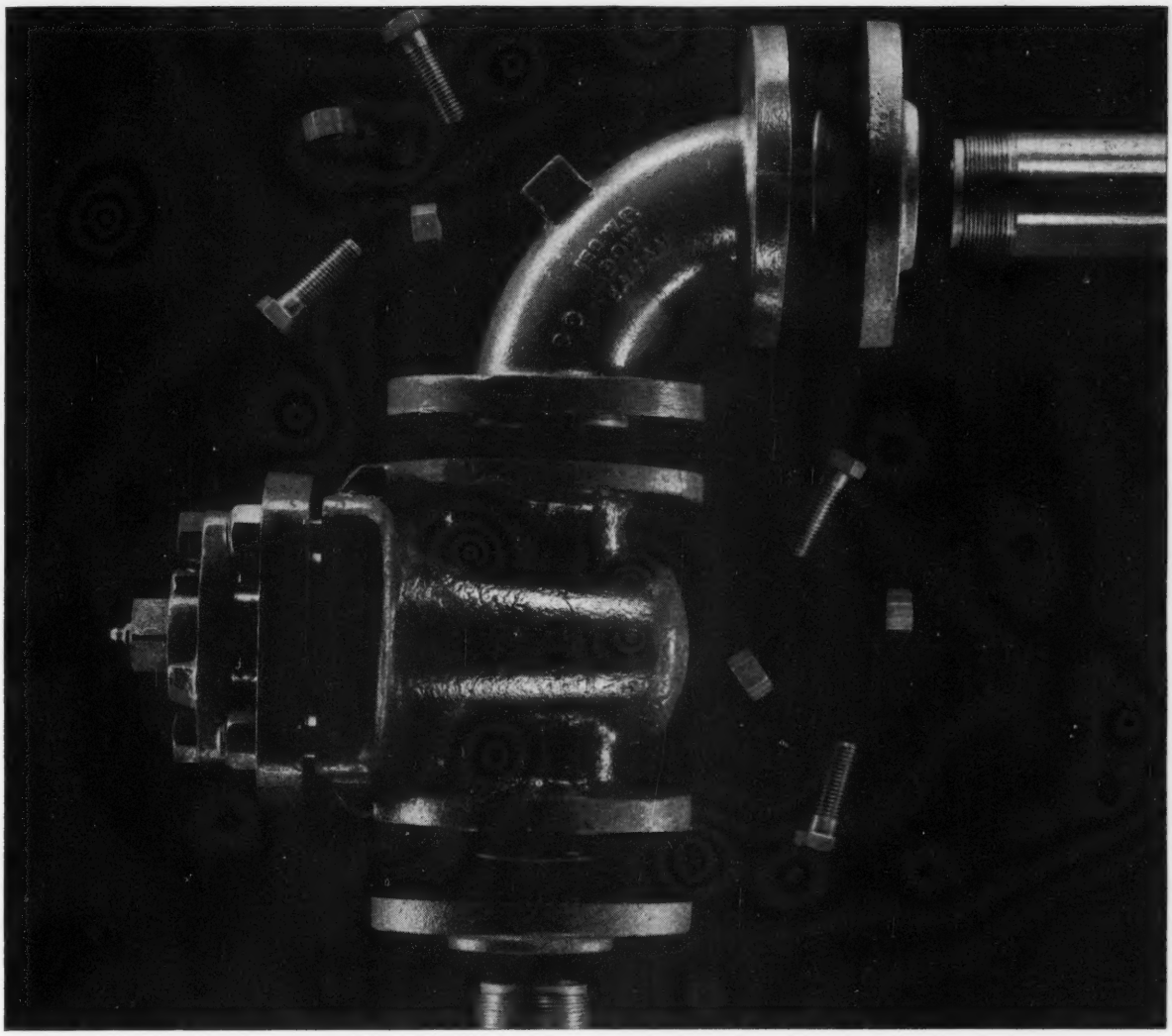
**Monel** netting used to hold insulation against boiler and steam line surfaces in a paper mill lasted 2½ times as long as galvanized steel netting.

•

**The Beryllium Corp.,** is operating at Hazleton, Pa. the nation's first integrated privately-owned plant for the fabrication of beryllium metal.

•

**Zirconium** was used by Pfaudler Co. to fabricate a shell and tube heat exchanger incorporating solid zirconium bonnets and tubes and zirconium lined tube sheets. The 4½ inch ID shell is made of Type 304 stainless steel. The resistance of zirconium to attacks by both acids and alkalis used alternately indicates it will find ready use in many industries.



# You can see why Saran lined pipe cuts operating costs

*These corrosion-resistant pipes, fittings and valves are stock items, and they can be fabricated in the field*

The long range economy of Saran lined pipe starts right here—with the immediate availability of pipe, fittings and valves . . . as stock items. There's no waiting . . . no price premium to pay.

And Saran lined pipe can be fabricated in the field. Only conventional hand tools or power equipment are needed to cut and thread it right on the job site.

Saran lined pipe pays off through the years with superior corrosion resistance and strength. When you specify the new gray Saran lined pipe, valves, pumps and fittings, you'll be able to pipe commonly used acids, alkalies and other corrosive liquids under a wider temperature range.

You can plan a *complete* corrosion-free pipe system with Saran lined pipe, valves, pumps and fittings. They're available for systems operating from full vacuum up to 300 psi and temperatures from −20° F to 200° F. Send the coupon today for further information. And be sure to ask about Saraloy® 898 tank lining, too. THE DOW CHEMICAL COMPANY, Midland, Michigan.

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FERNDALE 20, MICHIGAN

Please send me information on: ☐ Saran lined pipe, fittings and valves ☐ Saran lined centrifugal pumps ☐ Saraloy 898 chemical resistant sheeting

Name_____ Title_____ Company_____

Address_____ City_____ State_____

YOU CAN DEPEND ON DOW

## MEN in the NEWS

**Lloyd E. Raymond,** Singer Manufacturing Co., New York, was appointed to the staff of Robert W. Stewart, vice president in charge of production. Mr. Raymond will investigate new processes and developments in the field of investment casting, powder metallurgy and hard surface coatings. He is a member of NACE, and holds offices in the American Institute of Mining and Metallurgical Engineers and the American Society for Metals. He is also a member of the American Electroplaters' Society. Also appointed with him were **Franklin A. Park, Kenneth Perkins** and **Howard T. Peters.**

•

**Clarence Bremer,** a member of NACE, has been appointed technical director for Oakite Products, Inc., New York. He will be responsible for all of the firm's research, product development and technical service laboratory work.

•

**Richard W. Tannehill** will be in charge of technical activities at the Hycar nitrile rubber facilities of the Akron Chemical Plant of B. F. Goodrich Chemical Co. **Paul T. Whitmire** was named foreman of the general chemicals section.

•

**John W. Mayers** has been promoted to chief engineer of the Pittsburgh Coke & Chemical Co. He will be responsible for all design, construction and engineering activities of the company's plant facilities. The post is a newly created one.

•

**Mark W. Eichelberger,** executive vice president of the Lindsay Chemical Division of American Potash & Chemical Corp., died recently at Chicago. He was 58.

•

**Murray H. Bennett** is now president; **T. E. Detcher** vice president; and **E. A. Branche,** treasurer of Chemical Linings, Inc.

•

**W. G. Renshaw** and **R. A. Lula,** both of the research and development laboratory of Allegheny Ludlum Steel Corp., have been named joint winners of the Sam Tour Award of the American Society for Testing Materials. Mr. Renshaw is a member of NACE. He is research supervisor, corrosion section for his firm. A cash prize and certificates was presented to the men for their paper, Corrosion Properties of the Chromium-Nickel-Manganese Austenitic Stainless Steel, at the annual meeting of ASTM in Boston, June 25.

•

**Nicholas Chernik** has been promoted to assistant chief metallurgist of the Alloy Tube Division of the Carpenter Steel Co., Union, N. J. He now has supervisory responsibilities for the metallurgists in that department. His work covers the fields of corrosion, production, experimental and development problems and projects. He is a member of National Association of Corrosion Engineers.

•

**Marvin F. Hall** has been appointed consulting gas engineer for Ebasco Services Inc. He will be in charge of gas engineering activities for the engineering, construction and business consulting firm. He is a member of NACE and his firm is a corporate member of the association.

•

Ten field service engineers have been appointed to the nationwide sales force of A. M. Byers Co. They are: **R. E. Beisler** and **R. Spurgin,** Chicago; **N. J. Cremonese,** Silver Springs, Md.; **G. F. Grey** and **W. O. Williams,** Houston; **M. E. Hanley,** New York; **L. H. Hawks,** Boston; **E. M. Jones,** Pensacola, Fla.; **K. E. MacDonald,** Cleveland; and **L. L. Swaney,** Pittsburgh.

•

**E. S. Malkin** has been named eastern division manager and **J. F. Brauning** western division manager of the chemical products marketing group of National Carbon Co., Division of Union Carbide Corp. The two men will direct the field activities in their sales territories.

•

**George T. Deck** has been appointed vice-president and technical general manager of the renamed Lindsey Chemical Division, West Chicago, Ill. He had been plant manager for the American Potash and Chemical Corp. subsidiaries, American Lithium Chemicals, Inc. and San Antonio Chemicals, Inc., San Antonio, Texas. **Russell S. Sunderlin** succeeds Deck at the Texas plants.

•

**W. R. Wilkinson,** a senior vice-president of Johns-Manville Corp. has been made general manager of a Building Products Division which operates 12 plants and 13 sales offices in the United States. **J. A. O'Brien,** another senior vice-president, who was vice-president and general manager of J-M Industrial Products Divisions since 1955 was made vice-president for sales. **R. S. Hammond,** a vice-president of the Johns-Manville Sales Corp. has been appointed general sales manager of a new Industrial Building Products Sales Dept.

•

**G. H. Weight,** formerly Southwest District sales manager has been made sales manager, Middle states for The Babcock & Wilcox Company with headquarters in Chicago. **J. H. Roach,** of the Houston office was made district sales manager at the Tulsa office and **W. C. Mohrman** from the Tulsa office, becomes district sales manager for the Houston office.

•

**Walter P. Stroud** has been appointed plant engineer for American Viscose Corp. Film Division, Marcus Hook cellophane plant.

•

**James D. Ghesquiere** is now vice-president in charge of engineering for the Hinchman Corp. **David R. Loheit** is a new administrative assistant in the corporation.

•

**Kenneth Cooke Brownell,** 55, chairman of the board of American Smelting & Refining Corp. died August 4.

•

**Don M. Etter** has been given full responsibility for all sales operations of Cosasco Div., Perfect Circle Corp. **Leland Auer,** chief engineer remains in charge of production engineering and research and development while **Melvin Estey** will act in staff liaison capacity between Cosasco and its parent concern.

•

**Herbert C. Geittman, Jr.** an employee of Climax Molybdenum Co. died recently.

•

**George L. Illig, Jr.** has been named assistant to the vice-president of Industrial Chemical Sales, Hagan Chemicals & Controls, Inc., Pittsburgh. He is a member of NACE.

•

**Norman A. Fletcher** has been appointed manager of the valve division of Mineappolis-Honeywell Regulator Co.

•

**Arthur E. Bayce** and **Marvin A. Diesz** have been added to the professional staff of Shell Development Co., Emeryville, Cal. Mr. Diesz joined the polymer and chemical applications department as achemist and Bayce is a metallurgist in the materails engineering and corrosion department.


# EXPERIENCE

**"Theories are very thin and unsubstantial; experience only is tangible."**
**—HOSEA BALLOU**

Without the textbook theories, the student would have no starting point. Therefore, the theory is vital in that it provides the base upon which practice can be built.

But no theory is of any value until it has been proved or disproved by experience. And experience is gained in only one way—doing.

Mayes Bros. has been doing pipe coating and wrapping work for the last 28 years. In that time it has learned by repeated experience which theories are applicable to its operations and which are unacceptable.

Why not put this 28 years of experience to work for you on your next pipe coating and wrapping job? Mayes' jobs stand up, for they put permanence in pipe as promised.

1150 McCarty Drive

**MAYES BROS.**

**HOUSTON, TEXAS**

Tel. ORchard 2-7566

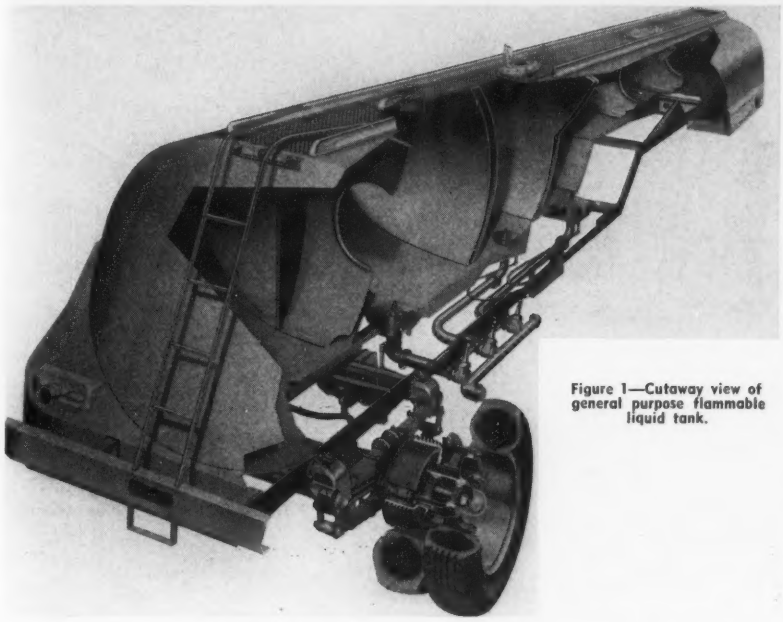

Figure 1—Cutaway view of general purpose flammable liquid tank.


## Abstract

This article considers some of the corrosion problems of the for-hire tank truck industry in its operation of about 26,500 tank vehicles.

General types of tank vehicles operated are described and illustrated, including those for transporting flammable and corrosive liquids and compressed gases. Materials of construction discussed include various types of steel, aluminum and clad materials. Use of metallic and organic coatings also is considered.

A brief outline of over 500 commodities being transported at wide ranges of temperature, viscosity and corrosiveness is given.

Operating conditions which affect corrosion rates, especially those that differ from those of fixed plant operations are discussed. Included are: Large percentage of empty "time"; wide variety of products transported in one tank; effect of prior products in combination with present product and results of cleaning methods on corrosion; inability to clean at time of unloading; and problems resulting from contamination of product by very small quantities of corrosive products.

Also discussed are corrosion problems ranging from the transportation of wine and hydrofluosilicic acid to the effect of brine solutions on city streets on aluminum tanks with steel under-carriages.


# Some Corrosion Problems of Tank Trucks And Their Solutions*

THIS ARTICLE deals in general terms with a subject which many believe is one of the most interesting fields of transportation and corrosion. It is a rapidly-developing and challenging field crowded with corrosion problems which so far have had little attention from corrosion engineers, principally because they have not been brought to their attention. This article may help to correct this situation and result in closer cooperation between corrosion engineers and the tank truck industry.

In recent years, that part of the trucking industry which is devoted to transportation of chemicals, gases and foodstuffs has expanded rapidly.[1] It is this phase of tank truck transportation most affected by corrosion.

In understanding the corrosion problems of the trucking industry, an understanding of the general nature and methods of operation of tank trucks is essential. First, the carriers are for-hire. That is, they will haul anything for which there is authority and equipment to handle safely, for anyone, to anywhere.

Because most chemical operations are subject to Interstate Commerce Commission regulations this article deals with operations regulated by the ICC. Carriers must obtain operating authority from the commission with respect to the commodities to be transported and places to be served. They also are required to operate specified types of tanks for commodities which the ICC classifies as dangerous.

There are operating today approximately 22,000 general purpose type units such as are familiarly known for gasoline transportation. Many of them also are transporting chemicals. Also operating are about 3500 so-called chemical tanks which are predominantly acid type or stainless steel tanks. Approximately 1000 tanks are transporting compressed gases.

All of these figures relate to over-the-road type tanks, predominantly semi-trailers, of over 3000 gallons capacity. General purpose type tanks average approximately 7000 gallons. These vehicles are, with some few exceptions, owned by the carriers.

### Types of Tank Motor Vehicles

Tanks may be divided into two general types: 1—Those transporting commodities which the Interstate Commerce Commission has classified as dangerous and, 2—Those used to transport commodities which are not so desig-

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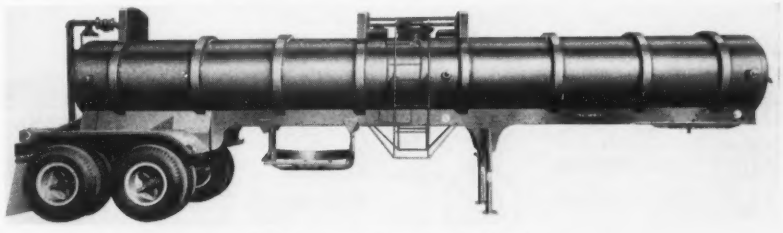

Figure 2—Ring Stiffener type acid tank.

★ A revision of the paper "Corrosion Problems of Tank Truck Transportation." by Louis Reznek, Director of Engineering and Safety, National Tank Truck Carriers Inc., Washington, D. C., presented at the 14th Annual Conference, National Association of Corrosion Engineers, San Francisco, California. March 17-21, 1958.

## Some Corrosion Problems–

(Continued From Page 105)

nated. This latter class may be further divided into sanitary type tanks and those not required to be of "sanitary" construction.

Three of the ICC dangerous articles classifications of primary interest are flammable liquids, corrosive liquids and compressed gases. Definitions for these classes and specifications for the tanks are to be found in the ICC Dangerous Articles Regulations. Rather than quote the definitions, a few illustrations of types of vehicles and a description of some commodities they customarily carry may be more valuable.

Figure 1 shows a cutaway view of a conventional tank used to transport flammable liquids such as gasoline, solvents and alcohols.

Note it is divided into compartments by transverse bulkheads and has baffle plates. While this is a conventional tank, the regulations under some conditions permit single compartment tanks and recently elimination of baffles has been authorized and internal or external ring stiffeners substituted for them. Primary purpose of eliminating bulkheads and baffles is to minimize corrosion and contamination. When these obstacles are eliminated, a "clean-bore" tank with no internal interference to proper cleaning, coating or lining can be operated. These tanks almost without exception are filled through manholes at the top and unloaded by gravity through bottom valves. They may be constructed of open hearth or blue annealed steel, high-tensile steel, stainless steel, or of various grades of aluminum. The choice depends upon cost, weight, contamination and corrosion factors.

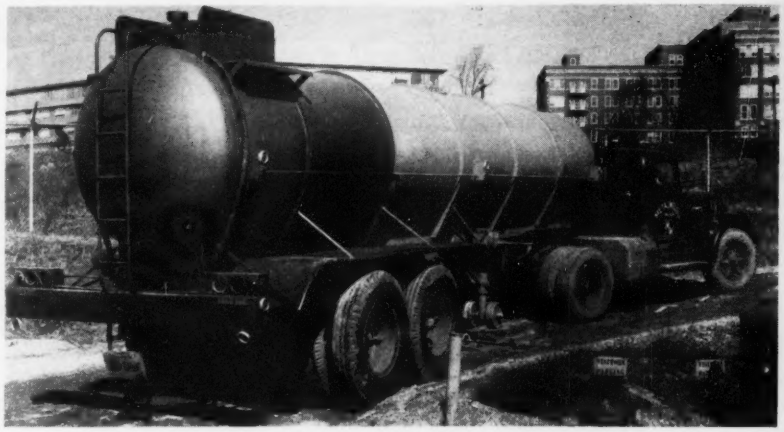

Figure 3—Acid tank with coating on spillage area.

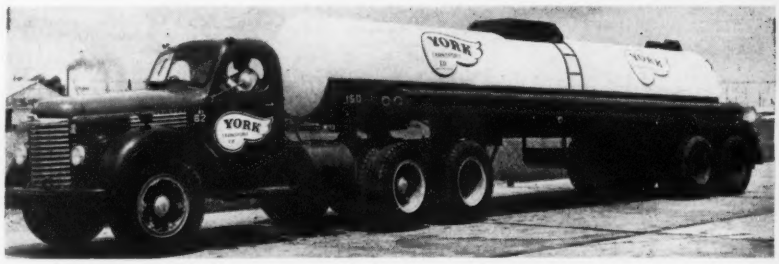


Figure 4—3000-gallon caustic soda tank vehicle.

Figure 2 shows a typical late-model tank for transporting corrosive liquids such as sulfuric, muriatic and nitric acids. These acids are top loaded. They are top-unloaded by air pressure. Note the tank is equipped with external ring stiffeners. This permits a cleanbore design. Former designs either were baffled for stiffness or of heavier construction. Internal restrictions did not permit ready lining with, for example, the rubber required for muriatic or weak sulfuric acid solutions. A tank of this general type in concentrated sulfuric acid surface may be constructed of as light as 3/16-inch steel.

Figure 3 shows an acid tank of somewhat older design. Such designs genreally were of ⅜-inch shell thickness. Note particularly the dam around the fill opening at the rear and the drainage tube to dispose of spillage. The problem of external corrosion from spillage generally has been more severe than internal corrosion in these acid tanks. Tanks of this type have been sandblasted and coated with 10 mils of specially catalyzed chlorosulfonated polyethylene in the rear area and 5 mils on the remainder of the tank. This is reported to be successful.

Figure 4 is a 3000-gallon caustic soda tank. These tanks are differently constructed than acid tanks because caustic soda is carried in concentrated solutions to avoid carrying water at no profit. The most concentrated of these solu-

(Continued on Page 108)

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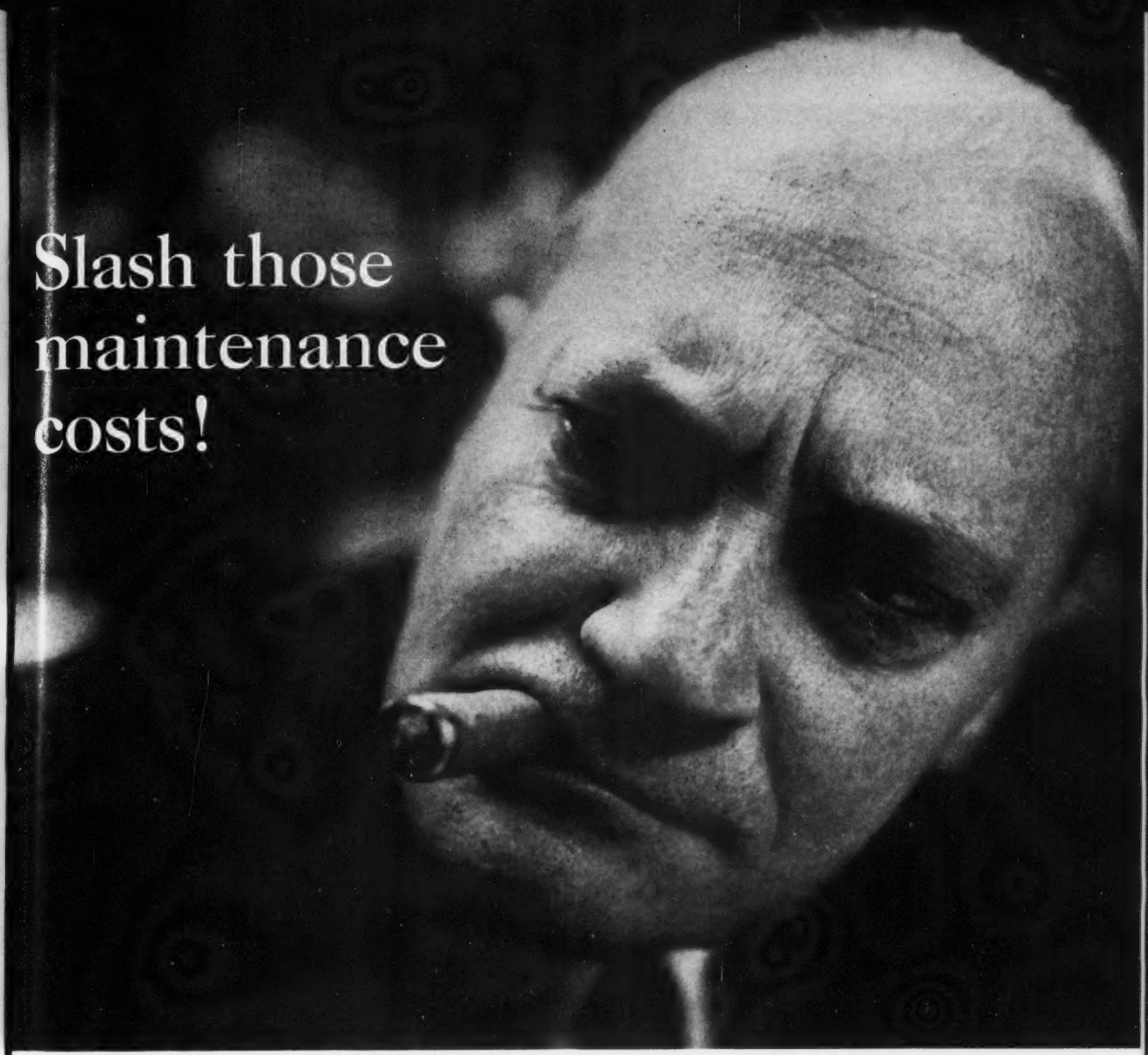


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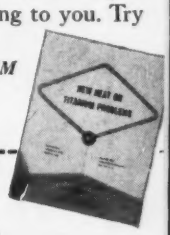

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Figure 5—Compressed gas tank vehicle.

## Some Corrosion Problems—

(Continued From Page 106)

tions may solidify at as high as 144 F. This means the material must be carried hot and that tanks must be insulated for long distance service. Because of its high viscosity, it may be and generally is bottom-unloaded. These tanks either are steam-coiled or, at least, have the outlet valve steam jacketed. In this service, aluminum is not used because of the corrosion problem.

Figure 5 is a compressed gas tank such as is used to handle about 15 types of liquefied gases. The principal gases transported are liquefied petroleum gas and anhydrous ammonia. These are American Society of Mechanical Engineers type vessels. From the corrosion standpoint there has been little difficulty because the specifications require all-steel valves and fittings on anhydrous tanks. Because they sometimes are used interchangeably between LPG service and anhydrous ammonia, care must be used in selecting valves. That is, the brass valves generally used when LPG is being transported must be removed. It is necessary also to be certain that the LPG is not contaminated by residual ammonia because contamination might cause corroded valves in cylinders where valves generally are brass.

Figure 6 shows a tank used to transport molten wax, which is not classed as a dangerous article. This is a stainless steel, steam-coiled, insulated tank. Typically it is used to transport wax to a plant manufacturing milk cartons. Although this is not strictly a sanitary type tank, corrosion, contamination or even over-heating which would cause discoloration would ruin the wax for this purpose because of the off-color.

### Types of Commodities Transported

The figures give only a general idea of the range of products carried. Currently over 500 commodities are being transported by tank vehicle; for instance:

Liquid oxygen at minus 270 F and molten phthalic anhydride at over 500 F.

Fluorine, chlorine, phosphorus, or sulphur.

Orange juice, syrup, milk and the plastic for dishes.

Pickles and peas, flour, cherries and caustics.

In short, practically anything that flows is capable of being transported by tank vehicle. If necessary it may be heated, cooled, pumped, blown or sucked.

### Operating Conditions Affecting Corrosion

One principal corrosion problem in which tank trucks differ from fixed plant type operations is when operating empty equipment. Unfortunately, from the profit and corrosion standpoints tank motor vehicles do not always run loaded, but are empty when moving almost half the time and are frequently standing empty in yards awaiting call.

This empty time does not always lessen corrosion rates because a thin film of many commodities will cause more corrosion than a full lading will. For example, an empty sulfuric acid tank open to atmosphere permits atmospheric moisture to dilute the film of acid to produce a much more corrosive film than if the tank were loaded.

Also because tanks frequently may be called upon to handle a wide variety of products, they are designed to handle as many different products as possible. An ideal solution would be a universal tank. Sometimes product moving in sufficient volume makes it possible to devote a particular tank to a particular service but this generally is not the case. A stainless steel tank costing $20,000 or more will be kept moving as much as possible by proper cleaning and designing for multiple-product operation. This means, from a corrosion standpoint, that a relatively expensive material such as stainless steel may be selected because it is useful for a wider range of products.

Some care must be exercised in shifting between products not only to be certain that none of the products will affect the tank or vice versa but also to prevent accidental chemical reaction between even small residues of a former load and the current load.

A few years ago two men who were cleaning a tank died after breathing fumes generated from a complex chemical reaction resulting from the effect of traces of oil from a prior trip which emulsified in combination with the aluminum shell and the residue of a load of weed killer compound.

The cleaning problem is complicated by the fact that the cleaning materials must not corrode the tank or have other harmful effects. For example, certain alkaline cleaners cannot be used in aluminum tanks. Only a few years ago

(Continued on Page 110)

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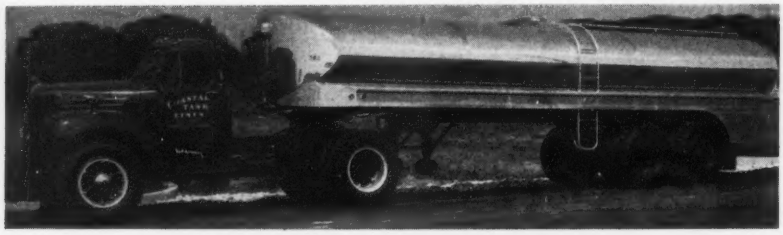

Figure 6—Stainless steel steam-coiled wax tank.

## Some Corrosion Problems—

(Continued From Page 108)

tank owners learned that they should never use conventional steel wool to clean stainless steel tanks because steel particles imbedded themselves in the stainless steel and started corrosion cells.

An ordinary muriatic acid tank is rubber-lined. The action of the muriatic acid on the rubber forms a surface coating which prevents further deterioration of the rubber and prevents corrosion. In order to improve the use factor on these tanks some carriers were washing them with chemical sprays and then using them to transport other materials. They found, to their dismay, that this removed the modified surface layer of rubber and the next load of muriatic acid had to form another layer. After this was repeated a few times the rubber-linings were gone and the tanks required major repairs.

### Cleanliness Is Essential

A few illustrations of the need for meticulous cleanliness may point out why even minute amounts of corrosion products is important. Tanks assigned to transport transformer oil were turned down because a test with a 5 gallon washout by the shipper revealed a single small piece of thread from the rags used to wipe down the tank. Even the slightest moisture on the walls of a tank is sufficient reason for a shipper to reject a tank for many products.

In the light of these examples it is obvious why contamination from corrosion is extremely important. A load of paint thrown off-color by corrosion may mean a loss of $10,000 and the loss of a load of penicillin by corrosion contamination may well run up to $100,000. It was serious to a carrier to the tune of $5000 last year—although somewhat amusing under the circumstances—when a load of maraschino cherries was spoiled because someone had failed to efficiently remove residue of a cargo of printer's ink the tank had transported earlier.

The next approach is to coat the tank with paints, plastics, resins, wax, rubber, glass, etc., in any one of hundreds of forms or formulations. This has been done and is highly successful for certain products. Generally coatings are not good enough to protect against a wide range of products. Baked phenolics have been particularly good in some services but are high-priced.

Experiments with tanks lined with Teflon and Kel-F show that while it is a very expensive solution the results may justify the cost because it is the closest approach presently known to a universal corrosion-proof material. Unfortunately, these materials have failed because they cannot be kept stuck to the shell. This problem is being worked on in the hope of an early solution.

The same corrosion problems are found in hoses, pumps, valves and other accessories as in the shells and they are being attacked in similar ways. One manufacturer has developed a Teflon-lined hose. He is making a market survey of the tank truck field because the prospective price in the sizes used by tank truck carriers is about $20 per foot.

The next approach to preventing corrosion is to clean the tank as soon as it is empty. There are available several excellent mechanical spray type and steam cleaners and several compounds which solve most of cleaning problems. This is not the final answer though because in the first place, the tanks have to be constructed so as to be capable of

(Continued on Page 111)

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effective cleaning. Second, although it is recognized that tanks should be cleaned immediately after unloading, it often happens the unloading point is hundreds of miles from the carrier's nearest terminal.

### Special Problems

The multiplicity of problems raised by the operating conditions previously mentioned have been solved largely by the combined action of shippers, carriers, tank truck manufacturers and the National Tank Truck Carriers, Inc. association.

Some recent problems were:

1. **Wine**—Can it be transported in aluminum tanks? In general, white wines were particularly affected for several reasons, including the change of dissolved sulfur dioxide to hydrogen sulfide.
2. **Hydrofluosilicic Acid**—Can stainless steel be used instead of rubber-lined tanks? Even stainless manufacturers were not prone to give outright recommendations because the corrosion rate depends to a large extent upon the care with which the tank is cleaned after being unloaded. So far, rubber-lined tanks are used for this commodity.
3. **Hydrogen Peroxide**—What materials and designs should be used for high-strength hydrogen peroxide such as used in missiles? Specifications limiting designs to certain specified aluminum alloys, with practically no copper content, have been drafted.
4. **Fertilizer Solutions**—what types of tanks are suitable? The answers here are not yet final because tests are still underway. In some cases stainless steels of certain grades are needed while in other cases aluminum of specific types is suitable also. The design also varies because of pressure considerations, the presence or absence of traces of sulfuric acid and ambient temperatures. There are so many types of fertilizer solutions and they change so often that carriers are running a close race with obsolescence because a new fertilizer may corrode the carrier's present tanks or rupture it from excess pressure.
5. **Phosphorus Oxychloride**—Is stainless steel an adequate replacement for a nickel-lined tank? While the regulations do not presently authorize stainless steels, a test vehicle is being operated to determine the answer to this question. In this connection a clad stainless tank was investigated and it was determined that in the thicknesses tested, stainless clad should not be used.
6. **Jet Fuels and Aviation Gasoline**—Can conventional steel tanks be used? Problems in handling these fuels for the military services arose out of requirements by some installations that such tanks should not be used for any product but gasoline or jet fuel. This resulted in corrosion of many tanks because the tanks were cleaned of oil films which prevented oxidation.

   In conventional service, carriers will carry a load of oil after carrying several loads of gasoline in order to get an oil film on the tank which reduces the rust problem. Many military installations have been requiring expensive stainless steel tanks, lined tanks, or aluminum tanks even though in many cases, the fuel is withdrawn from ordinary steel storage tanks and placed in similar tanks at the military base. Peculiarly, although two branches of the service welcomed aluminum tanks, another branch, up to a few months ago, prohibited aluminum refuelers claiming that aluminum in contact with aviation fuels under certain conditions formed a gel. This branch subsequently authorized aluminum.
7. **T-1 Steel and Anhydrous Ammonia**—The use of T-1 type steels for compressed gas tanks results in a saving of several thousand pounds. Because carriers generally estimate each pound saved is worth a dollar a year, the use of T-1 steel is economically attractive. Considerable reluctance to use T-1 steel in anhydrous ammonia service because of its copper content was—and is still to some extent—evident. Indications are, however, that proper fabrication and heat treating results in a tank which is not subject to corrosion.
8. **Electrolytic Corrosion**—Some corrosion problems, especially from salt solutions on highways during the winter, resulted from the use of steel undercarriages in combination with aluminum tanks. These problems have been overcome by proper design and washing after exposure.

(Continued on Page 112)


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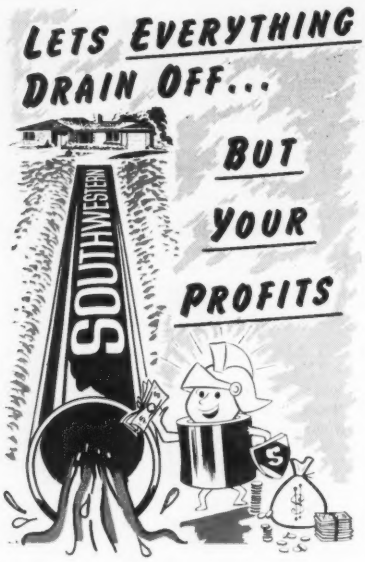


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## Some Corrosion Problems—

(Continued From Page 111)

### Solutions to Corrosion Problems

There are several methods of obtaining solutions to corrosion problems. The best and most obvious, but not necessarily the most economical solution is to use a material not affected by the commodities to be carried. This is possible for many commodities but the most useful material at present, stainless steel, imposes a price penalty.

Aluminum is good for many commodities and while it is at a price disadvantage its weight saving features often overcomes the higher price. Materials clad with stainless and nickel are no cheaper than solid stainless or nickel and often are high priced in the relatively thin gages used in tank transports.

#### Reference

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CORROSION's index appears in December.


## TECHNICAL REPORTS on Corrosion in Oil and Gas Well Equipment

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**TP-1** Report on Field Testing of 32 Alloys in the Flow Streams of Seven Condensate Wells (Pub. 50-3) NACE members, $8; Non-members, $10 per Copy.

**T-1C** Current Status of Corrosion Mitigation Knowledge on Sweet Oil Wells. A Report of Technical Unit Committee T-1C on Sweet Oil Well Corrosion. Per Copy, $.50.

**T-1C** Field Practices for Controling Water Dependent Sweet Oil Well Corrosion. A Report of Technical Unit Committee T-1C on Sweet Oil Well Corrosion, Compiled by Task Group T-1C-1 on Field Practices. Pub. No. 56-3, Per Copy $1.00.

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**TP-1O** Sour Oil Well Corrosion. *Corrosion* August, 1952, issue, only at $2.00 Per Copy.

**TP-1G** Field Experience With Cracking of High Strength Steel in Sour Gas and Oil Wells. (Included in Symposium on Sulfide Stress Corrosion.) (Pub. 52-3) Available only in Oct. 1952 issue of *Corrosion* at $2.00 Per Copy.

**T-1G** Sulfide Corrosion Cracking of Oil Production Equipment. A Report of Technical Unit Committee T-1G on Sulfide Stress Corrosion Cracking. Pub. 54-5. Available only in Nov. 1954 Issue of *Corrosion* at $2.00 Per Copy.

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# CORROSION ABSTRACTS


## INDEX TO CORROSION ABSTRACTS


Vol. 14 September, 1958 No. 9



Page

**3. CHARACTERISTIC CORROSION PHENOMENA**
- 3.5 Physical and Mechanical Effects....113
- 3.7 Metallurgical Effects .....114
- 3.8 Miscellaneous Principles .....115

**4. CORROSIVE ENVIRONMENTS**
- 4.3 Chemicals, Inorganic .....116
- 4.4 Chemicals, Organic .....116

**5. PREVENTIVE MEASURES**
- 5.3 Metallic Coatings .....116
- 5.4 Non-Metalic Coatings and Paints..118
- 5.9 Surface Treatment .....122

**6. MATERIALS OF CONSTRUCTION**
- 6.2 Ferrous Metals and Alloys.....124

**7. EQUIPMENT**
- 7.7 Electrical, Telephone and Radio....125

**8. INDUSTRIES**
- 8.3 Group 3 .....125
- 8.4 Group 4 .....126
- 8.5 Group 5 .....127
- 8.8 Group 8 .....127


## 3. CHARACTERISTIC CORROSION PHENOMENA

### 3.5 Physical and Mechanical Effects

3.5.6, 3.5.8, 6.3.15

**Porosity in Formed Titanium.** R. A. Wood, D. N. Williams, H. R. Ogden and R. I. Jaffee. Titanium Metallurgical Laboratory, Battelle Memorial Institute. U. S. Office of Assistant Secretary and Defense for Research and Development. May, 1957, 42 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121628)

A new type of material failure called "strain-induced porosity" has been found in parts formed of commercial-purity titanium. The phenomena was marked by surface pitting and internal voids formed in areas of the part which had been highly strained. A study of this phenomenon showed that deformation temperature, amount of strain rate, state of stress and amount and kind of impurity could affect the degree of porosity. The same kind of porosity has been found to occur in many other metals and alloys and it is believed to be a normal part of the mechanism of deformation in ductile materials.—OTS. 15151

3.5.8, 6.2.5, 4.3.6

**Stress Corrosion in Austenitic Steel by Nitrates.** O. Lissner. *ASEA J.*, **30,** No. 5, 85-91 (1957); *Engrs' Digest,* **18,** No. 12, 571-574 (1957) December.

Gives an account of investigations carried out as result of fracture of an end bell from a turbo-generator set. Study was made of the cracks, their origin, depth, appearance, nature and development in the steel. Microscopic examination showed that cracks progress in purely intergranular manner. Brittle fracture and fatigue tests showed that material had no great tendency to brittle fracture and did not yield especially low fatigue-resistance values. Stress-corrosion tests in various chloride reagents did not reproduce typical intergranular stress corrosion experience with the end bells. Stress-corrosion cracks were finally reproduced in solution of 36% calcium nitrate and 3% ammonium nitrate; bending stress of 19 tsi produced cracks in test sample from fractured end bell in 44 hours. Stress corrosion was shown to take place even in every dilute solutions of nitrate. Formation of nitrates could be attributed to corona phenomena and subsequent formation of ozone and oxidation of nitrogen. Precautions against stress corrosion include elimination of ventilating holes in end bells, use of stress relieving annealing, application of cathodic protection, e.g. varnish with high zinc content, and frequent inspection. New end-bell materials suggested by author include 12 chromium-12nickel-6 manganese-0.2 carbon steel and a nickel-free steel containing 12 chromium, 20-24 manganese and 0.08-0.20 carbon.—INCO. 15343

3.5.8, 7.1

**When Splines Need Stress Control.** D. W. Dudley. General Electric Co. *Product Eng.,* **28,** No. 25, 56-61 (1957) Dec. 23.

Discusses various stresses to be considered in designing to prevent spline failure, fretting corrosion as cause of wear and spline manufacturing processes. Charts and formulas are given for computing shear stresses in spline shaft, shear stresses in spline teeth, compressive stresses in spline teeth, and bursting stresses in internal spline parts. Splines have an area contact instead of line contact like gears and suffer from fretting corrosion rather than pitting and scoring as gears do. Badly worn spline, 3 inches in diameter, may have as much as 3 teaspoons of rust-like sludge from fretting between teeth. In some successful spline applications on aircraft engines, flexible coupling—without lubrication—may wear at rate of 0.010-inch in 1000 hours. In highspeed applications, over 10,000 rpm, fretting corrosion proceeds at 0.0001-inch per hour.—INCO. 15281

3.5.8, 8.10.3

**Fatigue in Mining and Construction Equipment.** B. M. Hamilton. Paper before Can. Inst. Mining & Met., Annual General Mtg., Ottawa, April, 1957. *Can. Mining & Met. Bull.,* **50,** No. 548, 717-724 (1957) Dec.

Nature of work involved subjects mining and construction equipment to vibration, heavy loading and shock loading. Most detrimental condition, however, is corrosion. Nature of operating stresses is reviewed and endurance limit is defined. S-N curves are shown for heat-treated SPS-245 steel (1.25 nickel-0.40 carbon-0.75 manganese-0.60 chromium-0.15 molybdenum). Discussion of effect of surface condition on fatigue properties covers surface finish, threads, decarburization, prestressing, corrosion and fretting. Explanation of nature of occurrence of corrosion fatigue is given. Typical examples of fatigue failure are presented and include: Fatigue fracture of steering linkage sector shaft of SAE 2340 due to heavy tool marks, corrosion fatigue in hollow drill steel due to aggravation by corrosive mine water and fretting fatigue in tapered bit end connection of hollow drill steel.—INCO. 15295

3.5.8, 6.4.2

**Fatigue Properties of Aluminum Alloys.** G. Forrest. **Chapter from the book** "The Fatigue of Metals," edited by J. A. Pope. *Sheet Metal Inds.,* **34,** No. 367, 831-845 (1957) Nov.

An account is given of the fatigue properties of aluminum alloys as shown by rotating beam or reversed flexure tests. The alloys are divided into groups and their properties related to their general mechanical and metallurgical characteristics. General comments are

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made on notch sensitivity and the behavior of some alloys with respect to notches is described. It is shown that material with a low yield stress may, under certain circumstances, give longer life than one with a high yield stress. The effect on fatigue behavior of internal or residual stresses is described and it is shown that these stresses can have very large effects both by increasing or reducing the properties according to their direction. The effect of aluminum cladding is shown to reduce the fatigue properties of sheet material under certain circumstances but with high mean stresses or with very sharp stress concentrations, little effect is noted. Under corrosion fatigue, the fatigue strength of all the alloy is reduced; the behavior does not appear to be related to their relative corrosion resistance (without fatigue). Finally, the fatigue properties are considered in relation to various "production" variables. (auth.)—ALL. 15255

**3.5.8, 6.3.6, 7.2**

**Fatigue Properties of Brasses, Bronzes and Bearing Metals.** J. W. CUTHBERTSON. Chapter of Book "Fatigue of Metals", edited by J. A. Pope, Chapman & Hall, Ltd. *Metal Treatment & Drop Forging,* **24,** No. 138, 139, 89-92, 159-161, 168 (1957) March, April.

Form of fatigue curve and fatigue properties of copper-base alloys are considered, while greater part of article deals with fatigue properties of bearing metals. Table summarizes fatigue and tensile properties for 90/10 and 70/30 brasses, Naval brass, Admiralty brass, 95/5 bronze, manganese bronze aluminum bronze, Monel, copper-beryllium and Superston bronze. Fatigue limit of 50,800 psi for Superston bronze (9.73 Al-4.97 nickel-5.42 iron-balance copper) is highest value for any material other than high-tensile steel. Service requirements for bearings and mechanism of bearing failure are discussed with references to Babbitt metal. Chief alternatives to tin-base Babbitt are discussed; these include lead-base Babbitt, copper-lead alloys, aluminum-tin alloys, composite bearings (such as Durex made by sintering 85 Cu-15 nickel powder on steel backing) and electrodeposited silver bearings.—INCO. 15245

**3.5.8, 5.5.3**

**Fretting Corrosion as an Engineering Problem.** K. H. R. WRIGHT. *Corrosion Prevention and Control,* **4,** No. 11, 37-44 (1957) Nov.

Description of characteristics and mechanism of fretting corrosion. Use of surface treatments and lubrication in reduction of fretting is discussed. Most suitable greases to use for lubricating a ball race subject to fretting conditions appear to be those which have a high shear susceptibility, thus enabling an oily phase, resulting from breakdown of gel structure of grease, to be available on race itself. Relationship between fretting corrosion and fatigue is demonstrated with tests on aluminum alloy. Graphs, photos.—INCO. 15210

**3.5.8**

**Corrosion Fatigue.** T. D. WEAVER. Paper before Soc. Chem. Ind., Bristol Sec. Dec. 6, 1956, *Chem. & Ind.,* No. 36, 1190-1194 (1957) Sept. 7.

Discusses definition of corrosion fatigue, effects of mechanical and chemical notches, methods of testing, effect of test variables (test speed, temperature, corrodent strength, oxygen content) on data, the mechanism of corrosion fatigue, corrosion-fatigue resistance of various materials and surface protection against corrosion fatigue. Tables show: Effect of temperature corrosion-fatigue resistance of mild steel; air and corrosion-fatigue resistance of bronzes, steels and stainless steels; effect of various protective coatings on corrosion-fatigue-resistance of 3 steels; and effect of nickel and chromium plating on air-fatigue properties of Armco iron, low-carbon steel, nickel-chromium steel, aluminum-copper-nickel alloy, copper-chromium alloy, medium-carbon steel, chromium steel, nickel-chromium steel, nitrided chromium-molybdenum steel, carburized nickel-chromium steel and Duralumin.—INCO. 15137

**3.5.9, 6.3.20, 6.3.9, 6.3.5**

**"Exotic" Metals Look Good for Tomorrow's High Temperature Structures.** I. STAMBLER. *Aviation Age,* **28,** No. 3, 42-47 (1957) Sept.

The "exotic" metal of today is the workhorse material of tomorrow. Molybdenum and niobium are now being studied intensively for the over 1600 F. temperature range. Main problem with niobium is oxidation resistance but since it doesn't have a volatile oxide, there should be a better chance of stabilizing it than there is with molybdenum. Niobium should prove useful at temperatures 600-700 F above the optimum range of nickel base alloys. Niobium is also attractive because its density is about the same as that of nickel or cobalt. Proper use of alloying elements, such as zirconium, can reduce the oxidation rate. The only series that has shown good tensile properties over a wide range of compositions is vanadium-titanium. Another promising alloy class is vanadium-carbon. These alloys have only marginal ductility at room temperature, but at high temperatures they are capable of as much as 10% elongation. They can be forged, though with difficulty. Zirconium is the ninth most abundant metal in the world; it is rare only because extraction is difficult. Major advantage of zirconium is excellent corrosion resistance and it can be cast, rolled, forged, extruded and machined. However, zirconium is very sensitive to the absorption of hydrogen and its hardness drops rapidly with heating, as do its mechanical properties. Tables, graphs.—INCO. 15055

**3.5.9, 6.3.16, 6.3.9**

**A Survey of Metallic Materials for High-Temperature Service.** J. T. STACY. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-T-1, April 10, 1948 (Declassified Feb. 20, 1957), 38 pp. Available from Office of Technical Service, Washington, D. C.

A brief review is given of materials for high-temperature service which covers particularly the strengths of the various materials at elevated temperatures for service lives of one hundred or one thousand hours. Short discussions of a few high-temperature tests, types of high temperature alloys and the dependability and commercial availability of some of these alloys are given. The usefulness of tungsten and molybdenum at high temperatures is considered. Various properties, such as corrosion resistance, weldability, thermal expansion and deformation are discussed. Recommendations are made concerning alloys most suitable for service above 1500 F. (auth)—NSA. 15068

## 3.7 Metallurgical Effects

**3.7.3**

**New Techniques Solve Welding and Brazing Problems with PH Steels.** F. K. LAMPSON. Marquardt Aircraft Co. *SAE J.,* **65,** No. 13, 37-38 (1957) Dec.

Discusses techniques being used to overcome following problems encountered in welding and brazing precipitation hardening steels: cracked welds and low weld ductility, oxidation of aluminum during welding process, crevice corrosion of brazed joints and unsatisfactory bonds from normal brazing operations. References are made to 17-7PH, AM 350, 355 and A-286.—INCO. 14984

**3.7.3**

**Shielding Gases for Inert-Gas Welding.** W. H. HELMBRECHT AND G. W. OYLER. Linde Co. Paper before Am. Welding Soc., Nat'l. Fall Mtg., Cleveland, Oct. 8-12, 1956. *Welding J.,* **36,** No. 10, 969-979 (1957) Oct.

Discussion of shielding gases has included inert gases (argon and helium) as well as addition of active gases (hydrogen, oxygen, nitrogen and carbon dioxide) to argon primarily. Arc characteristics, flow rate and weld quality obtained with each gas or gas mixture have been summarized for each metal (aluminum, mild steel, stainless steel, high temperature alloys, copper, nickel, nickel alloys, magnesium and titanium) and for each inert-gas process whether used with manual or mechanized operation. Graphs show effect of arc power on welding speed, effect on arc potential of adding hydrogen to argon and to helium and arc voltage-arc length curves for various gases, all pertaining to tungsten-arc welding of stainless steel. Cross-sections of butt welds and tube welds made in 16-gage stainless steels using various gases are shown. Table presents corrosion data for Type 347 welded with either 347 or 321 electrodes. Recommended shielding gases for consumable electrode welding of nickel, Monel and Inconel are tabulated. —INCO. 14915

**3.7.3, 5.3.4**

**Hot Pressure Bonding.** S. STORCHHEIM, *Metal Progress,* **72,** No. 1, 97-101 (1957) July.

A hot pressure bonding is useful in the cladding of a wide variety of metals for industrial purposes. Metallic pairs which normally form brittle and unusable metallics at higher temperatures of fusion welding can be bonded with great strength and corrosion resistance even though these same brittle alloy zones appear in the microstructure. Since the pressure applied is hydrostatic, any of the strong intermetallics which form do not ordinarily develop microfractures. Considerable data have been acquired on the joining of aluminum and nickel by this technique. An experimental apparatus, which is a small scale replica of that used for production purposes, consists basically of a high-temperature die surrounded by an induction furnace, both placed in a water-cooled chamber which can be evacuated. Pressure is applied to the top of the chamber by a ram moving through a Wilson seal. Temperature is measured by thermocouples located in the die and punch near the samples. The temperature itself is controlled by means of a variable transformer. Into the die is slipped a closely fitting round slug of aluminum, a disc of nickel of the same diameter and a second slug of aluminum. Then the top part of the die

chamber is filled with a punch. The tank is evacuated to less than 5 microns and the desired compacting pressure put on the ram for the correct time. After reversing the cycle the bonded slugs are removed and are ready for machining into test pieces. A number of bimetallic systems have been studied by this process based on aluminum with nickel, copper, iron and zirconium. From the results it is concluded that hot pressure bonding offers a quick, inexpensive reproducible high quality method for cladding one metal with another.—ALL. 15064

**3.7.3, 5.3.4, 6.3.10**

**The Onera Process of Skin Annealing in a Gaseous Atmosphere.** P. GALMICHE. *La Recherche Aeronautique*, No. 59, 27-32 (1957) July-August; *Engrs.' Digest*, **18**, No. 8, 345-347 (1957) Aug.

Based on fact that corrosion cracking of high-temperature (turbine blade) nickel-chromium alloys of modified 80/20 type, is assocated with local deficiency of chromium, new Onera skin-annealing process (which includes annealing cycle of rapid heating, holding at temperature and rapid cooling), is performed in two ways. One is chromizing treatment producing very slight, uniform and controlled increase in chromium content of surface layers; and other, a bright-annealing treatment which increases homogeneity of chromium in surface layer by removing, in form of volatile fluoride, some of titanium which is main cause of corrosion under action of combustion gases. Graphs show change in chemical composition of surface layers of Nimonic 95 as function of distance below surface (work of F. Malamand). —INCO. 14893

**3.7.3, 6.2.5**

**Brazed Stainless Sandwich Spot-Welded.** J. C. HERR, R. C. SMITH AND G. L. PETERMAN. *Am. Machinist.*, **101**, No. 1, 127-129 (1957).

Stainless-steel honeycomb structures were brazed in an inert atmosphere at 1450 F (790 C), using an 85:15 silver-manganese alloy. The brazing alloy had no detrimental effect on the strength or corrosion-resistance of the weld.—MA. 14906

**3.7.4, 3.7.3, 6.3.15**

**Investigation of Beta Phase "Recrystallization" in Titanium-3% Aluminum-5% Chromium Alloy.** K. B. LLOYD AND E. J. CHAPIN. Naval Research Lab. Nov., 1957, 22 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order: PB 131338).

An important problem in the development of heat treatment procedures for improving properties of titanium alloys has been the accelerated grain growth which occurs when the metal is heated through the allotropic transformation. This study was conducted to explore the possibility of controlling the beta grain size during heat treatment of binary and ternary titanium alloys with aluminum and chromium and to determine the resulting effects on mechanical properties. Among the results, it was observed that the binary titanium-aluminum alloy compositions did not form networks of small beta grains when heat treated just below their transus. Absence of this characteristic prevented control of beta grain growth during heat treatment. Networks of small transformed beta grains were obtained in the microstructures of both the binary titanium-chromium series and the ternary titanium alloy series. Chromium promoted the formation of small beta grains at temperatures just below the transus in both binary and ternary alloys. In all samples, tensile properties were not affected by differences in either microstructure or heat treatment.—OTS. 14975

## 3.8 Miscellaneous Principles

**3.8.4, 3.5.9, 6.3.5**

**Oxidation of Niobium Between 375 C and 700 C.** EARL A. GULBRANSEN AND KENNETH F. ANDREW. Westinghouse Research Labs., Pittsburgh. *J. Electrochem. Soc.*, **105**, 4-9 (1958) Jan.

Niobium has been found to oxidize in a complex manner. At 400 C and lower a slow rate of reaction is observed with the kinetics following the parabolic rate law. At a weight gain of 55 to 70 $\mu$ g/cm$^2$ a transition in the kinetics occurs to a nearly linear rate law. Between 550 and 625 C the oxidation rate is nearly constant as a function of temperature, while above 625 C the oxidation rate again increases with the temperature. The adherence of the oxide is poor above the transition point. (auth.)—NSA. 15165

**3.8.4, 4.3.2, 6.3.6, 6.2.2, 6.3.8**

**Dissolution of Copper, Iron, and Lead in Nitric Acid. Part I.** A. G. LOSHKAREV. *Zhurnal Prikladnoi Khimii* (J. Applied Chem.) USSR., **30**, No. 10, 1558-1564 (1957). Available from Associated Technical Services, P. O. Box 271, East Orange, New Jersey.

Rate of dissolution in 2.60-13.0 N nitric acid at 17-37° is found limited by rate of solvent diffusion to the surface


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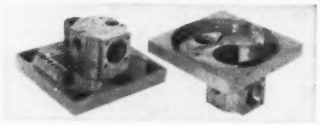

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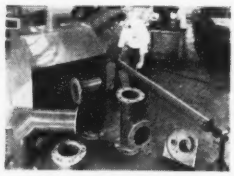

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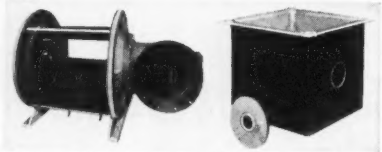

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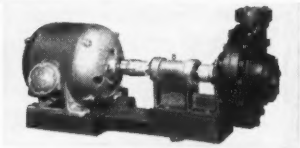

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of the metal. 1 table, 7 figures, 10 references.—ATS. 15350

3.8.4, 6.2.2, 4.3.2

**Kinetics of the Dissolution of Iron in an Acid Medium. Pt. I. Action of Adsorbed Hydrogen.** (In Italian.) Liliana Felloni and Giampaolo Bolognesi. *Annali di Chimica*, **47**, 985-995 (1957) Sept.

Dissolution tests in hydrochloric acid at 25 C were conducted on samples of Armco iron of various thickness-area ratios. It appears, from analysis of the results, that the reaction consisting of combination of hydrogen atoms takes place at active points on the metal surfaces. The process of absorption, which occurs at different points, after achievement of a dynamic equilibrium inside the metal, appears to influence the total process of dissolution of iron and evolution of hydrogen either as a result of polarization, through attainment of a certain maximum speed of diffusion, or as a result of a change, caused by absorption in the crystal lattice. 17 references.—MR. 15251

## 4. CORROSIVE ENVIRONMENTS

### 4.3 Chemicals, Inorganic

4.3.2, 6.2.3, 6.2.5

**The Corrosion of Steels by Hydrochloric Acid in the Spheroidal State.** Kh. L. Tseitlin and S. M. Babitskaya. *Zhurnal Prikladnoi Khimii* (J. Applied Chem.) USSR, **31**, No. 1, 84-89 (1958). Available from Associated Technical Services, Inc., P. O. Box 271, East Orange, New Jersey.

Action of hydrochloric acid droplets separated by a hydrochloric acid-water film from the base metal (carbon & stainless steels) was studied at 200-500 C. 2 tables; 1 figure; 6 references.—ATS. 15250

4.3.5, 3.8.4

**The Reduction of Oxide Films by Atomic Hydrogen.** M. R. Piggott. Imperial College, London. *Acta Crystallographica*, **10**, 364-368 (1957) May.

The reactions of atomic hydrogen with thin films of oxides of copper, iron, lead and nickel were investigated, using electron diffraction to determine the crystalline state and composition of the film before and after the action of the atomic hydrogen. No reduction was observed in the case of iron and nickel oxides, while complete reduction was observed with the copper and lead oxides investigated. The crystalline state of the metal after reduction was found to depend on the concentration of the atomic hydrogen, i.e. upon the speed of the reaction. (auth.)—NSA. 15000

4.3.7

**Corrosion of Metals by Hydrogen Sulfide at High Temperature.** (In Russian.) Kh. L. Tseitlin, L. V. Merzloukhova and V. A. Strunkin. *Zhurnal Prikladnoi Khimii*, **30**, No. 10, 1553-1558 (1957) Oct.

Corrosion stability of metals subjected to the action of hydrogen sulfide and its mixtures with water, steam and nitrogen at various concentrations.—BTR. 15104

### 4.4 Chemicals, Organic

4.4.5, 8.4.3

**Effect of Oil Field Use of Chlorinated Solvents on Catalytic Reforming.** J. A. Guthrie and P. S. Hepp. Sun Oil Co. *Refining Engr.*, **29**, No. 13, C-40, C-44 (1957) Dec.

Use of chlorinated solvents in oil fields has led to serious catalyst deactivation and equipment corrosion problems in catalytic reformers. Type and magnitude of troubles encountered due to chloride contaminated feed are outlined. Once organic chlorides are converted to hydrochloric acid in the reformer it is possible for hydrochloric acid to pass through a variety of refining equipment and to cause extensive corrosion with accompanying rapid equipment failure, particularly where moisture is present. Greatest assurance of compatibility with refining operations can be obtained by using additives or solvents containing only hydrocarbons. Graphs.—INCO. 15274

4.4.8

**The Corrosion Effects of Protein-Type Foam-Forming Concentrates on Common Metals and Dissimilar Metal Couples.** H. B. Peterson and J. C. Burnett. U. S. Naval Research Laboratory, June, 1957, 22 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 131018).

This study was concerned with the corrosion effects of four protein-type foam concentrate materials currently used for fire-fighting on common construction metals. Stainless steel 304 was most resistant and brass, copper, steel and aluminum followed in that order of descreasing resistance. Effects on galvanic couples were also studied. Aluminum was anodic to all metals except zinc and magnesium. Steady-state electrical current measurements were good indicators of relative intensity of corrosion.—OTS. 15023

4.4.10

**The Behavior of Materials in the Presence of Formaldehyde.** (In German.) E. Lignau. *Werkstoffe u. Korrosion*, **8**, 480-487 (1957) Aug.-Sept.

Properties, production and applications for formaldehyde. Literature review is given of action and reaction of formaldehyde on and to aluminum and aluminum alloys, carbon and alloy steels, non-ferrous metals and alloys, inorganic materials, and synthetic materials. Supporting data are included on nickel, nickel-copper alloys, Types 302, 304, 316, 317, 347, Durimet T, Worthite, Monel, Inconel and Hastelloy C.—INCO. 14978

## 5. PREVENTIVE MEASURES

### 5.3 Metallic Coatings

5.3.4

**Electroplating from the Pyrophosphate Bath. Pt. 1. Electrodeposition of Single Metals.** T. L. Rama Char. *Electroplating & Metal Finishing*, **10**, No. 11, 347-349 (1957) Nov.

Investigations carried out in author's laboratory have shown that tin, copper, zinc, nickel and lead can be satisfactorily plated from pyrophosphate solutions; optimum plating conditions are listed for each case. Preliminary work indicates that bath may also be useful for electrodeposition of cobalt and iron. Results are summarized with respect to addition agents, polarization and anodes. Advantages of pyrophosphate solutions over conventional baths are given. 29 references.—INCO. 15036

5.3.4

**The Physical Properties of Electrodeposited Metals.** T. E. Such. *Metallurgia,* **56,** Nos. 334, 335; 61-66, 121-124 (1957) Aug., Sept.

Importance of mechanical properties of electrodeposit in wear resistance, fatigue resistance, forming and drawing, electroforming, corrosion resistance, and polishing is discussed. Most critical properties of plated metals are tensile strength, ductility, hardness, and internal stress. Influence of codeposited materials (metallic or non-metallic), problem of hydrogen embrittlement, phenomenon of internal stress and effect of basis metal on mechanical properties are considered. Influence of both solution composition and operating conditions on properties of chromium, copper, nickel and zinc are considered in detail. Methods available for determining tensile strength, ductility, hardness and internal stress are discussed. Many references are made to nickel plating, and data for nickel plate are presented in numerous tables and graphs. 30 references.—INCO. 15069

5.3.4, 6.2.2

**Hot Dip Aluminizing Widens Cast Iron Uses.** J. D. Sprowl and G. E. Speicher. Kaiser Aluminum & Chemical Corp. *Iron Age,* **180,** No. 6, 87 (1957) Aug. 8.

An aluminum coating applied by a simple new hot-dipping process makes cast iron much more resistant to heat and corrosion. This increased protection will permit use of less costly gray and malleable irons in applications currently limited to highly alloyed types. Application of coating is following by heat treatment at 1700 F. During this treatment aluminum diffuses completely into the iron and produces a coating composed entirely of iron-aluminum alloy. This heat resistant coating protects cast iron indefinitely from scaling in sulfurous and other environments at temperatures up to 1400 F. Photomicrograph.—INCO. 15105

5.3.4, 7.7

**Aluminum-Sheathed Power and Telephone Cables.** Friedrich Otten. *Z. Metallkunde,* **48,** No. 5, 245-249 (1957).

A general review: Methods of sheathing; corrosion-resistance and its enhancement by the external application of bitumen, rubber and PVC coatings, physical and mechanical properties; electrical characteristics; laying and jointing; technical and economic advantages over lead-sheathed cables. 22 references.—MA. 15026

5.3.4, 3.2.2

**Vacuum Deposition Avoids Embrittlement.** V. Dress. Lockheed Aircraft Corp. *Iron Age,* **180,** No. 25, 142-145 (1957) Dec. 19.

There is no danger of hydrogen embrittlement when steel parts are cadmium plated by vacuum deposition. Moreover, cadmium coatings applied in this way can meet all military specifications for adherence, corrosion resistance and other key properties. Using standard vacuum chambers and pumps, cadmium deposits 0.0003-0.0005-inch thick can be maintained uniformly and thicker coatings can be had if desired. Throwing power of process is excellent, yielding almost completely uniform layers on high spots and recessed areas alike. Photos, photomicrograph.—INCO. 15211

5.3.4, 6.3.17, 4.6.2

**Development and Properties of Uranium-Base Alloys Corrosion Resistant in High Temperature Water. Part II. Alloys with Protective Cladding.** I. Cohen, R. K. McGeary, W. A. Bostrom and R. A. Wolfe—I. Cohen and E. L. Losco, Editors. Westinghouse Electric Corp. U. S. Atomic Energy Commission Pubn., WAPD-127 (Pt. II), Sept. 7, 1955 (Declassified Sept. 24, 1957), 159 pp. Available from Office of Technical Services, Washington, D. C.

Several gamma phase uranium-molybdenum and uranium-niobium alloys and one epsilon phase uranium-silicon alloy, which had been shown to have good corrosion resistance in high temperature water and steam when tested in the bare condition, were selected for study of their corrosion behavior when clad with Zircaloy-2 by extrusion. Simulated rod-shaped fuel elements from the extrusions were used to investigate the corrosion resistance of the fuel alloy and the mechanism of failure as affected by the presence of the bonded cladding. Corrosion life tests were performed on these samples, and detailed results are given. An investigation was also made to determine the major factors responsible for variations in corrosion life and results indicate that these are pimpling of the cladding at the site of the defect caused by a localized build-up of oxide at the base of the defect, discontinuous


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cracking of the fuel in γ phase core alloys with subsequent rapid corrosion of the fuel and rupture of the cladding, and formation of corrodible core-clad inter-diffusion layers. Heat treatment after extrusion and its effect on the corrosion was investigated. A study was also made of the interdiffusion of core and cladding. The effects of other variables, such as cold drawing, size of cladding defects, cladding thickness and end plug design on corrosion behavior were investigated.—NSA. 15227

**5.3.4, 6.3.17**

**Vapor Deposited Zirconium on Uranium.** CARROLL F. POWELL, ROBERT P. JONES, FLEET T. GIROD AND IVON E. CAMPBELL. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-1018, July 20, 1955 (Declassified Feb. 14, 1957), 30 pp. Available from Office of Technical Services, Washington, D. C.

Low-carbon uranium was given protective coatings by packing the specimen in zirconium and subjecting it to iodine vapor at 0.5 to 15 mm mercury pressure at 1050 C. The most protective of the coatings was obtained with a 24 hr. treatment, giving coatings 3 to 13 mils in thickness. Good coatings were formed only at 1000 C or above. Coating compositions fell in the range $UZr_{0.7-3}$. The protection afforded by these coatings in 100 C water was highly variable, with exposure periods ranging from 200 to 600 hr., averaging 300 hours, before accelerated corrosion occurred. Higher carbon uranium (0.04 to 0.05 wt.% carbon) zirconized readily only when prealloyed with 1 wt.% of zirconium. Coating periods from 3 to 6 hr. gave good coatings only on specimens alloyed with 0.35 at.% chromium or 1 wt.% zirconium. Such specimens consistently showed low corrosion rates [0.001 to 0.016 mg/(cm²)(hr)] over 300 to 500 hr. periods. Coated specimens had a coarse grain structure and this was not refined in the few instances where coated specimens were heat treated. The minimum corrosion rate exhibited by pack-zirconized coatings was about 0.0003 mg/(cm²)(hr). General intergranular penetration of the coating by water vapor appeared to set the maximum low-corrosion period obtainable with a 10-mil-thick pack-zirconized coating at around 2000 to 3000 hr. (auth.)—NSA. 15383

**5.3.4, 6.2.2**

**Spray Galvanizing as a Means of Rust Protection on Iron Poles.** (In German.) ERNST ZAMZOW. *Elektrotechnische Zeitschrift*, **9,** Ausgabe B, 359-361 (1957) Sept.

After sandblast cleaning of iron parts, a 0.1-mm-thick zinc layer is sprayed on. Any weak spots that may develop during the following few weeks are treated with zinc paste. Then the poles are painted twice with a paint which should be free of lead and acid.—BTR. 15177

**5.3.4**

**The Behavior of Materials During Electroplating.** I. H. HEFELE. *Metalloberflache*, **11,** 368-370 (1957) Nov.

Investigation of behavior of brass during silver, nickel, or nickel and chromium plating and of steel during hard chromium plating, to elucidate observations made in works practice. Study was made of lead segregation in the α-matrix of brass sheet and of β-phase and their effect on bright chromium plating involving nickel underlay.—INCO. 15307

**5.3.4**

**Zinc as a Corrosion Protector and Its Use on Finished Products.** (In German.) H. PETERS. *Metall*, **11,** No. 8, 670-672 (1957) Aug.

The author reviews the uses of zinc, with particular reference to its application as a corrosion protector for iron and steel. Hot dip galvanizing is said to be the most economical method of protecting ferrous metals. Where this process cannot be used, sherardizing is most suitable for small articles such as nails, screws, etc., but zinc plating is preferred where precision is necessary. Zinc spraying is recommended for large parts such as bridges and ships.—ZDA. 15391

**5.3.4, 6.3.17**

**Research on Corrosion Resistant Coatings for Uranium. Interim Report Covering the Period of February 1952 to February 1953.** C. E. LACY, A. P. BEARD, C. J. BECK, W. D. DAVIS, W. L. ROBB AND G. E. GALONIAN. Knolls Atomic Power Lab. U. S. Atomic Energy Commission Pubn., KAPL-952 (Del.), Declassified with Deletions Feb. 26, 1957, 65 pp. Available from Office of Technical Services, Washington, D. C.

A general survey was made of possible techniques for applying a bonded, protective coating to uranium using a boiling water test to evaluate the coating quality. Of the techniques studied the most promising methods for applying such a coating were electroplating with nickel, vapor plating with zirconium, evaporation of chromium and extrusion cladding with zirconium. (auth.)—NSA. 15348

**5.3.4**

**New Plating Process for Corrosion and Wear Resistance.** *Industrial Finishing*, **9,** 921-926 (1957) Nov.

Chemical process (Kanigen) deposits a hard, uniform, nonporous and highly corrosion and wear resistant nickel-phosphorus alloy with a number of unusual properties.—MR. 15326

**5.3.4, 6.3.17**

**Protection of Uranium: Vapor-Deposited Coatings.** I. E. CAMPBELL, E. M. SHERWOOD, C. F. POWELL AND R. P. JONES. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-887, Nov. 24, 1953 (Declassified Feb. 25, 1957), 20 pp. Available from Office of Technical Services, Washington, D. C.

The most satisfactory vapor-deposited coatings on uranium were obtained by a displacement-diffusion process similar to pack chromizing, employing the vapors of the lower zirconium iodides. Coatings of zirconium-uranium alloy up to 5.9 mils thick were obtained during a 24-hr treatment at 1050 C. These coatings, of undetermined composition, were adherent, non-porous and exhibited corrosion rates in boiling water of the order of 0.001 to 0.006 mg/cm² hr. The average life of the coatings in boiling water is about 500 hours. Chromium was deposited on uranium by thermal decomposition of $CrI_2$ vapor. Niobium was deposited by hydrogen reduction of niobium chloride vapor at reduced pressure. Molybdenum was deposited by thermal decomposition of molybdenum carbonyl. Zirconium was deposited by thermal decomposition of, or displacement from, zirconium tetraiodide vapor by disproportionation of the vapors of lower zirconium iodides ($ZrI_2$ + $ZrI_3$) and by reduction of the lower zirconium iodides with magnesium and zinc vapors. This latter group of coatings was unsatisfactory because of porosity, poor adhesion, or the presence of the underlying salt deposits. (auth.)—NSA. 15261

**5.3.4, 8.9.2, 6.2.5, 6.4.2**

**New Plating Methods Offer Improved Decorative Parts.** H. MAHLSTEDT. Metal and Thermit Corp. *Automotive Inds.*, **117,** No. 11, 65, 114 (1957) Dec. 1.

Two new metals which have received much attention for auto trim parts are stainless steel and aluminum. Stainless steel parts are chromium-plated to match color of plated die castings and to keep stainless itself from tarnishing. Method of bright anodizing aluminum alloys has been announced but these do not have same color as chromium-plated parts. Among most promising developments is bright crack-free chromium plating; corrosion resistance increases with thickness of plate until optimum of 100 millionths of an inch is obtained. Progress in developing plating corrosion tests resulted in acetic acid salt spray, accelerated acetic acid salt spray and Corrodkote tests; review is given.—INCO. 15361

## 5.4 Non-Metallic Coatings and Paints

**5.4.2**

**Ceramic Coatings Raise Heat Resistance of Super-Alloys.** P. A. HUPPERT. Gulton Industries, Inc. *Iron Age*, **180,** No. 20, 157-159 (1957) Nov. 14.

Ceramics available today offer heat-corrosion resistance in 2000-2500 F range; indications are that they can be compounded to go a good bit higher. New refractory materials such as boron nitride and special fluxes (lithium compounds) make it possible to apply thin ceramic coatings that will even improve high temperature properties of superalloys. Tables list physical, mechanical and electrical properties of boron nitride, lithium compounds and lithium salts available, properties of lithium compounds in so-called ceramic family and compositions of complex lithium compounds.—INCO. 14919

**5.4.2, 4.3.3**

**Some Experiments in Comparing the Resistance of Enamels to Corrosion by Alkaline Solutions.** H. B. KIRKPATRICK, E. L. MCGANDY AND J. C. RICHMOND. Paper before Am. Ceramic Soc., 55th Ann. Mtg., New York, April 27, 1953 (Revised June 1957). *J. Am. Ceramic Soc.*, **40,** No. 11, 389-395 (1957) Nov.

Describes investigation of corrosion of enamel surfaces by alkaline aqueous solutions, with immediate objective of contributing to establishment of standard test apparatus. Experiments are described which show effects of solution temperature, concentration, container material and specimen position on rate of dissolution of titania-opacified sheet-steel enamel and cast-iron enamels. Results indicate that in designing apparatus to measure corrosion rates, solution temperature should be controlled to at least ± 0.1 C, that no glass parts of apparatus be exposed to alkaline solution and that, in absence of stirring, consideration be given to positioning of specimens. Apparatus consists of stainless steel beaker and lid fitted with immersion heater, stirrer, reflux condenser and wells for thermometer and thermo-regulator. Specimens are placed in small holders vertically around walls of beaker, exposing only 1 side to solution. All parts in contact with solution are Type

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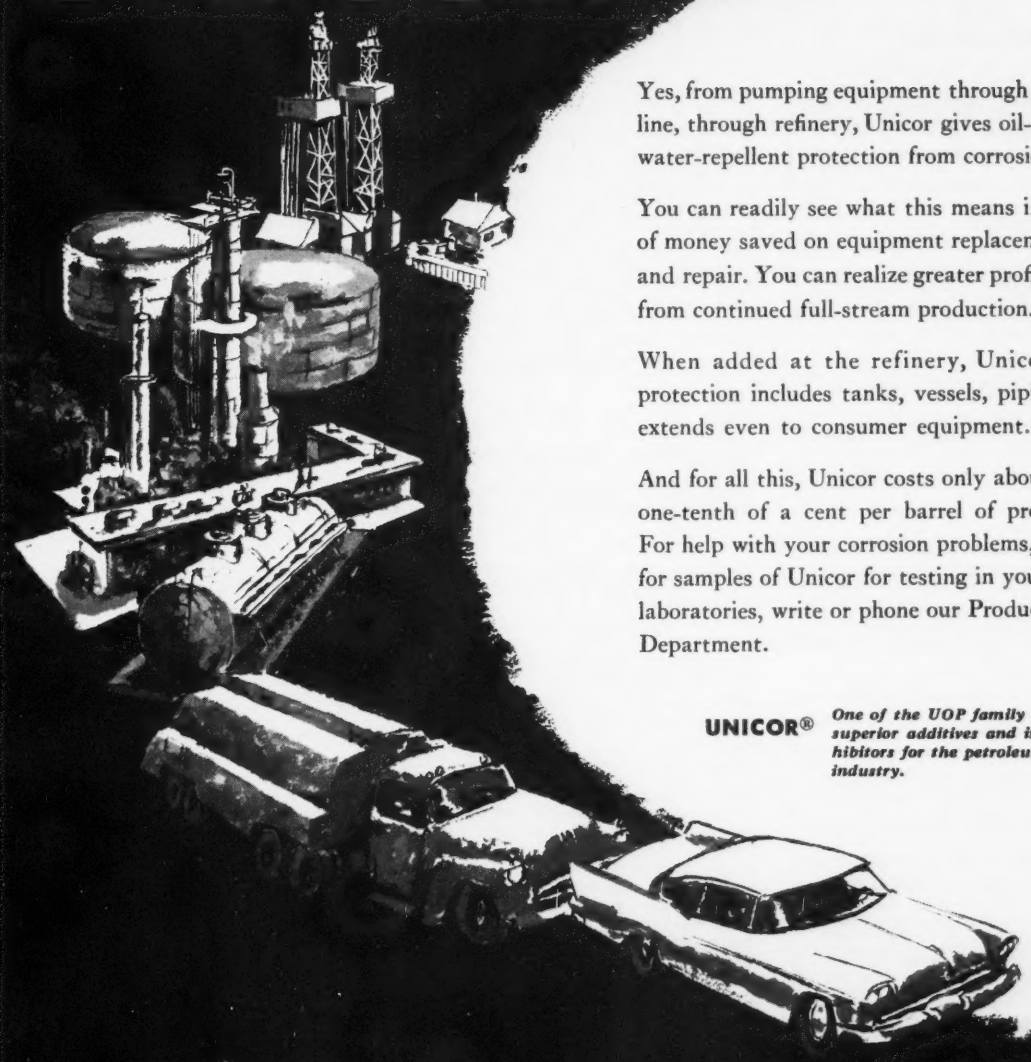

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304; immersion heater is chromium-plated copper. In case of cast-iron specimens, areas of exposed iron were nickel-plated to prevent rusting. Weight-loss and silica-loss data are shown in tables and graphs.—INCO. 15344

5.4.3, 6.2.5

**How to Select Chrome-Moly Steels for Ball and Rod Mill Liners.** T. E. NORMAN. Climax Molybdenum Co. *Eng. Mining J.*, **158**, No. 7, 102-106 (1957) July.

Covers properties, fields of application and comparative wear resistance of chrome-moly liner steels. Steels are classified as pearlitic and martensitic. Fabrication and heat treatment are discussed. Resistance to plastic flow is considered. Peening action on wearing face of chromium-molybdenum steel grate bars prevents plugging by worn balls in grate ball mill. Suggestions are given to serve as guide in selection of material for mill liners and in testing program. Table gives relative wear rates of various liner materials when tested as 5-in grinding balls in ball mill at Climax. Table includes martensitic high-chromium-molybdenum white irons, martensitic high-carbon chromium-molybdenum steels, martensitic 4 nickel-chromium white iron, pearlitic high-carbon chromium-molybdenum steel and austenitic (Hadfield) manganese steel. The nickel-chromium iron is used quite successfully in many mills in spite of its low toughness.—INCO. 15011

5.4.5, 8.9.3

**Three Kinds of Pipe Protection are Being Applied on NGP's Major Project.** P. REED. *Oil & Gas J.*, **55**, No. 49, 98-100 (1957) Dec. 9; *ibid.*, No. 50, 134, 136, 138 (1957) Dec. 16; *ibid.*, No. 52, 223-224, 227 (1957) Dec. 30; *ibid.*, **56**, No. 2, 117-118, 120 (1958) Jan. 13.

An interesting and significant comparison of established and new pipe-protection materials can be found on Natural Gas Pipeline Co. of America's 350 mile main line from Bridgeport, Texas, across Southern Oklahoma to Fritch, Texas, coal tar, asphalt and plastic tape are being applied on different sections. It was found necessary to have all asphalt-coated pipe wrapped with kraft paper to hold coating to pipe and prevent sagging in warm weather. Both coal-tar and asphalt coatings are wrapped with glass mat which is embedded as near center of hot coating as practicable. Cold plastic paint was applied at approaches to overhead stream crossings, at some valve and at some short places on pipe. Photos.—INCO. 15043

5.4.5

**Are Lead Pigments Unnecessary in Anticorrosive Paints?** H. HEBBERLING. *Werkstoffe u. Korrosion*, **8**, No. 6, 345 (1957).

The unique properties of red lead, viz., its special activity at weak points in the primer film and its independence of the nature of the medium for maintenance of eletrochemical protective action are the subject of comment.—RPI. 15308

5.4.5, 6.4.2

**Protective Varnishing (Aluminium and Aluminium Alloys).** (In French.) JEAN-JACQUES MEYNIS DE PAULIN. *Rev. Aluminium*, **34**, No. 245, 757-765 (1957) July-Aug.

A number of varnishes of various types are described which can be used with good results for the preservation of the bright appearance of finished aluminum surfaces. The adherence of these varnishes to aluminum subjected to different pretreatments and their resistance to aggressive substances, such as gasoline, p'aster and concrete was tested. From the results of these studies it is concluded that varnishing provides effective protection for decorative components of motor cars and for aluminum products in architectural application.—ALL. 14928

5.4.5

**Synthetic Elastomers in Corrosion Prevention.** (In French.) E. S. VOUTETAKIS. *Corrosion et Anticorrosion*, **5**, 244-252 (1957) Sept.

Elasticity, wear resistance and chemical resistance of elastomer-based coatings after vulcanization. The use of Neoprene-based paints and of chlorosulfonated polyethylene (Hypalon).—BTR. 15138

5.4.5

**Materials of Construction—Protective Coatings.** F. SCOFIELD Nat. Paint, Varnish & Lacquer Assoc. *Ind. & Eng. Chem.*, **49**, No. 9, Pt. 2, 1639-1642 (1957) Sept.

Reviews recent literature on newer coating systems (epoxy resin, urethane, silicone, vinyls, rubber, miscellaneous resin, alkyd, latex, emulsion and zinc-rich types), surface preparation and corrosion, specialty coatings (fire retardant, heat-resistant, fungicidal, temporary and strippable), paints for woods and application and curing. 148 references.—INCO. 15084

5.4.5

**Vinyls as Metal Finishes.** C. I. SPESSARD. *Ind. Finishing*, **9**, No. 105, 469 (1957).

An outline of methods for the evaluation of vinyl coatings; greatly improved adhesion is claimed by the use of a maleic-modified resin, a vinyl butyral wash primer or a primer based on hydrolyzed vinyl chloride resin. Some performance tests and their results are mentioned.—RPI. 15058

5.4.5

**Polyesters for Surface Coatings.** E. J. MURRAY. *By Gum*, **28**, No. C-3, 4-11, 14 (1957).

Polyesters containing either styrene or vinyl-toluene as the reactive monomer requiring the addition prior to application of an organic peroxide as a curing agent are discussed. Cobalt napthenate or dimethyl-aniline incorporated with the polyester or added with the organic peroxide component initiate the peroxide decomposition to free radicals and accelerate the curing time. The applications of these coatings on metal, masonry and wood are reviewed.—RPI. 14992

5.4.5

**Treatment of Galvanized Surfaces.** Leyland Paint & Varnish Co. *Paint J.*, **7**, No. 53, 444, 460 (1957).

The pretreatment and priming of zinc-coated surfaces are briefly described. Cadmium primer can be directly applied to galvanized surfaces after suitable degreasing. Priming paints containing graphite or metallic pigments (other than zinc) should be avoided. Primers based on red ferric oxide, micaceous ferric oxide, zinc dust and blends of zinc oxide are recommended. Where the surface is recognized to be porous, two coats of primer are recommended.—RPI. 14980

5.4.5

**Mastics for Corrosion Control.** W. W. HENDERSON. *Tappi*, **40**, 216A-219A (1957) Sept.

Mastic as corrosion control coatings in all industries using steel, tankage and iron or steel equipment; types and uses of Erkote mastics; recommendations for pretreatment of surfaces and for application of mastica.—MR. 14888

5.4.5

**Zinc Dust as a Pigment in Protective Paints.** (In German.) M. HOCHWEBER. *Schweiz. Arch. angew. Wiss. u. Technik*, **23**, No. 6, 169-174 (1957) June.

The use of zinc in protecting steel structures against corrosion is briefly considered and the literature on zinc-dust pigmented paints is reviewed. The author's practical experience in the use of such paints indicates that excellent


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corrosion resistance can be obtained in environments which are not directly corrosive to zinc, on clean surfaces free from loose rust and scale, provided the paint is applied with skill and care. The color is not unlike that of the unpainted steel and inspection particularly of multiple coatings would be facilitated by the addition of dyes. The paints are not poisonous and can be sprayed and painted components can be welded without danger to the operator. A minimum thickness of 60 $\mu$ is recommended; in very corrosive atmospheres 200 $\mu$ should be used. The paints are specially suitable for covering and repairing galvanized surfaces.—ZDA. 14905

**5.4.5, 3.5.4, 2.3.2**

**Methods of Accelerated Weather Deterioration for Fluorescent Paints.** F. M. NOONAN AND J. E. COWLING. U. S. Naval Research Laboratory. Nov., 1957, 23 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 131302).

The usefulness of daylight fluorescent paints depends largely on their ability to resist color change and deterioration of fluorescence caused by weather, sunlight in particular. To aid in the development of more stable high-visibility paints, an accelerated test method was developed to distinguish between "light-stable" (six-months durability) and less stable paint formulations. The report presents an adequate performance specification for daylight fluorescent red-orange paint. The proposed specification was based on a method involving laboratory exposure to a carbon arc which simulated "sunshine" and induced approximately the same degradation in 275 hours as would result from approximately four months of Miami, Florida weather exposure. A simple photometer-type instrument was designed for evaluation of fluorescence of paints. A change of filter in the instrument also permits measurement of color fading.—OTS. 15027

**5.4.5, 5.2.1**

**The Painting of Cathodically Protected Surfaces.** D. M. MACDONALD. *Chemistry in Canada*, **9**, No. 9, 64, 66, 68, 70 (1957) Sept.

Corrosion theory and the theory of cathodic protection are briefly outlined to illustrate the necessity of using alkali resistant paints for coating surfaces protected by magnesium anodes. On a cathodically protected surface the hydroxyl ions are produced within the paint film, which therefore must be chemicaly inert to alkali. It is pointed out that paint is necessary, even when the surface is cathodically protected, since: (1) paint provides sufficient in-


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sulation to maintain the necesary potential without the use of excessive currents; (2) topcoats contain poisons to prevent marine organisms from attaching themselves, the latter causing increased drag with consequent increased fuel consumption. Tests on a series of resin based paints, the vehicles of which contained no chemical groupings of atoms which could be split by bases, have been conducted. From the tests, two paint systems appear superior, i.e.: (1) a widely used proprietory material and (2) a material containing vinyls. The proprietary paint system had a considerably shorter antifouling life than the vinyl. Both systems are presently used in the (Canadian) Navy. Better paints for this type of service are being developed by testing the newer resins as they become available. Resins presently under test include: Epoxys, methacrylates, crylates and chlorosulphonated polyethlenes. The use of different pigments chiefly in vinyl based paints is also being examined. Exposure tests on panels treated with copper and graphite, instead of cuprous oxide, the usual antifouling pigment, have been undertaken. The use of certain metallic pigments in the priming paint are being tested. A series of paints developed by Australian scientists which dry by reacting with water, have been tested. The vehicle is prepared by the reaction: $TiCl_4 + 4C_4H_9OH + 4NH_3 \rightarrow Ti(OC_4H_9)_4 + 4NH_4Cl$. The product is known as butyl titanate and reacts with water to produce a form of titanium dioxide. This reaction is illustrated by: $Ti(OC_4H_9)_4 + 2H_2O \rightarrow TiO_2 + 4C_4H_9OH$. Some difficulties were encountered in finding an additive which would prevent hydrolysis of butyl titanate. The following summarizes the recommended practices for painting cathodically protected structures: (1) Surface preparation should be the best possible. (2) The metal should then be protected with phosphoric acid or vinyl wash primer. (3) The paint should not contain oil unless a long period of atmospheric exposure will occur before immersion. (4) Vinyl paints appear best if considerable attention can be paid to preparation of a homogeneous film. (5) When recoating is necessary, if it is not possible to remove old paint by sandblasting, the use of bituminous base paints may prove more satisfactory.—ALL. 14974

5.4.5

**Zinc-Rich Paints Protect Iron and Steel Parts.** R. J. FABIAN. *Materials in Design Engineering*, **46**, No. 1, 102-104 (1957) July.

This article discusses zinc-rich paints of both organic and inorganic types. Their resistance to chemicals, including acids and alkalis, salt and fresh water and temperature are briefly described and general information is given about formulation and methods of application. Zinc-rich paints are said to have been used successfully on refrigeration equipment, water tanks, dam gates, oil pipelines, cooling towers and many other steel structures exposed to corrosive atmosphere or to water. 5 illustrations. —ZDA. 15265

5.4.5, 8.9.3

**High Density Asphalt Mastic Coating.** N. L. BROWN. Paper before ASME, Petroleum-Mech. Eng. Conf., Tulsa, Sept. 22-25, 1957. *Gas Age*, **120**, No. 11, 37, 40-42, 45 (1957) Nov. 28.

Description of development and application of a Timcoat coating that is a combination protective and weight coat to be used on pipelines laid primarily in marsh, swamp and off-shore areas. Coating mixture consists of coarse and fine aggregates, a rubberized asphalt binder and an internal and external reinforcement with combination of ingredients being varied to suit various laying conditions or requirements. Application process allows welding, coating and lowering of some 4800 ft. of 12¾ in. pipe in a 10-hour work day on a cost basis competitive with that of enamel and concrete coatings.—INCO. 15191

5.4.5

**The Effect of Fillers on the Properties of Bituminous Anticorrosion Coatings.** (In Russian.) V. I. Zhukov and A. A. Kozlovskaia. *Stroitel'. Predpriiatii Nefti. Prom.* (Building Enterprises of the Petroleum Industry), **2**, No. 8, 11-14 (1957) Aug.

The M-IV bitumens used for an insulating mastic are saturated with water. Degree of saturation depends on the mineral part present in the bitumen. Highly-plastic bitumens are recommended for obtaining coatings with high operating durability. Limestone, crumb rubber and P-200 polyisobutylene are suggested as fillers.—BTR. 15175

5.4.5

**Epoxy Resins in Surface Coatings.** L. M. BARAKAN. *Paint Manuf.*, **27**, No. 8, 308-313 (1957).

The physical and chemical properties of surface coatings based on epoxy resins are described and formulations are suggested for special finishes. Details are also given of the types of catalysts which may be used, the production of oxidizing and plasticizing esters, methods of reacting with amino and phenolic resins and the manufacture of paint based on catalyzed epoxy resins. 13 references.—RPI. 15202

5.4.5, 6.2.3

**Steelworks' Maintenance Painting.** W. J. CHALMERS. *Corrosion Technology*, **4**, No. 6, 195-197 (1957) June.

This article, which describes briefly the conclusions reached after 15 years' experience of painting a steelworks, mentions the successful use of a zinc-rich primer. The conventional red lead primer was attacked by acid moisture while drying, but the zinc-rich primer dried rapidly enough to be unaffected. A red oxide/zinc chromate primer based on a synthetic resin was also found to be useful. Two illustrations.—ZDA. 15196

## 5.9 Surface Treatment

5.9.1

**Surface Preparation.** Pt. VII. J. SNELLING. **The Decorator, 56**, No. 663, 39-40 (1957).

Filling compositions, the properties and advantages of various types, and their application, are reviewed.—RPI. 15066

5.9.1, 6.4.2, 6.4.3

**Chemical Surface Protection of Light Metals.** (In German.) A. POLLACK. *Metall*, **11**, No. 9, 754-756 (1957) Sept.

A comprehensive survey of various methods of surface treatment developed for the corrosion protection of aluminum and magnesium is presented. The review begins with the discussion of processes first introduced by Jirotka, Pacz and McCulloch, stating that they no longer have practical significance. This is followed by a treatment of the Protal, MBV, EW, Alodine, Iridite, Alprox and the wash primer processes. The methods of chemical surface treatment applicable to magnesium are divided into 3 main groups: (1) Oxide films which consist either entirely or chiefly of magnesium oxide; (2) Fluoride coatings with magnesium fluoride as a main component; (3) Other protective substances such as selenium or magnesium selenide. 17 references. —ALL 1510[illegible]

5.9.3, 7.1

**Investigation of the Applicability of High Frequency Sound Waves (Ultrasonics) for Cleaning of Precision Parts.** O. E. MATTIAT AND P. P. ZAPPONI. Clevite Research Center. U. S. Wright Air Development Center, June, 1957, 76 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 131361.)

Accessible soils of all kinds are shown to be easily removed from small precision parts by the ultrasonic systems studied. Inaccessible soils, such as steel particles in bearings and grease in blind holes, require high sonic intensities and a coupling fluid with optimum cavitating and solubility or dispersability properties for the particular soil. Low frequency systems appeared more effective than high frequency systems for removing most soils investigated. Those included greases, burnt-on carbon, lapping and buffing compounds, steel particles and a synthetic soil. It was further observed that bearing damage resulting from ultrasonic treatment is insignificant for the short cleaning times normally required. Processes are recommended for cleaning precision parts and bearings. A coupling fluid—trichloroethylene—is shown to be best for removal of soils. The steel-removal and probe methods, two new processes for evaluating ultrasonic systems and factors are described.—OTS. 15025

5.9.3, 8.9.1

**Forming Integrally Stiffened Wing Panels by Shot-Peening.** KENNETH SPARLING. *Machinery*, **91**, No. 2344, 903-906 (1957) October 18.

During the past year shot-peen forming has been applied to large integrally stiffened wing panels at Lockheed Aircraft Corporation, Burbank, California, USA. Forming is accomplished by the impact of 0.093-in. diameter cast-steel shot which is directed against the flat surface to produce a convex shape. The shot is propelled by high-velocity jets of air and makes small indentations in the surface of the aluminum. Residual compressive stresses ranging up to 50,000 lbs./sq. in. are thus induced in a layer about 0.020-in. deep at the surface of the material. In consequence, the area of the peened surface tends to increase and the workpiece is caused to bend. As the work bends, the opposite concave surface is also subjected to compression until the stresses in the two surfaces are in balance. A 40-ft. long panel can be shot-peen formed in approximately three hours (this formerly took more than 24 man hours when using hot bending methods) and only simple flat templates for typical contours along the length of the panel are

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required, so that cooling costs are low. The curvature of any particular portion of the panel is controlled by alternating the peening intensity and the degree of saturation. The aluminum alloy used is 7075-T6. To avoid risk of corrosion and to remove any foreign material the parts are cleaned with a mild caustic solution immediately after the peening operation. The panels then receive an Iridite corrosion-resistant treatment in readiness for painting and assembly operations. Mechanical properties of alloy are not greatly altered by shot-peening. The fatigue strength is improved slightly. Corrosion resistance is greatly increased because of the residual compressive stress in the surface of the peen-formed part. The Lockheed peen-forming machine has an overall length of the bed exceeding 85 ft. All forming takes place within a rubber-lined peening cabinet which covers a 4-ft. length of the workpiece.—ALL. 15073

5.9.3

**Removing Rust and Scale by Abrasive Cleaning.** E. JACOBSON. *Organic Finishing,* **18,** No. 6, 9-11 (1957)

An outline of the main classes of airless abrasive blasting equipment is given, together with some examples of suitable applications of the method and advantages to be gained from its use. —RPI. 15318

5.9.4, 2.3.2

**Black Oxide Coatings on Steel: Quality Tests.** J. Doss. Rock Island Arsenal Lab. *Electroplating and Metal Finishing,* **10,** No. 9, 289-290 (1957) September.

An oxalic acid spot test was found to provide good indication of black oxide coating quality in case of 12 out of 13 types of steel investigated. Panels were treated in aqueous alkaline oxidizing bath for various periods of time and both ground and sandblasted surfaces were investigated. Drop on good quality coating acquired black or brown color in 3-8 minutes whereas that on poor coating became grey in under 3 minutes. An inhibition test, humidity cabinet test and spot tests using solutions of citric acid or ammonium citrate were unreliable.—INCO. 14931

5.9.4, 6.4.4

**Progress in Surface Treatment of Magnesium Alloys.** (In French.) G. SIEBEL. Office National d'Etudes et de Recherches Aeronautiques, Paris, France, Publication No. 5, page 45, 1957.

The anodic processes, Elomag, Flussal and Seomag, which have been developed and used in Germany, have for some time been widely used by industry. With reference to the anodic process for producing protective coatings on magnesium alloys, it can be said that, with suitable post-sealing treatment, they represent considerable improvement as compared with the non-electrolytic processes. The anodic process is not, however, as good as has been attained with aluminum alloys by the anodizing process, the reason for which can be ascribed mainly to the different chemical and physical characteristics of magnesium, compared with aluminum and its chemical compounds. In the opinion of the author, an anodic treatment of magnesium alloys can only be considered primarily for pressure die cast parts for the optical and photographic industries. There exists in addition, a possibility of application of the anodic treatment process with cast parts which are particularly subjected to corrosion or wear, however, not for sheets which have to be further handled and processed after the surface treatment, as the anodic coatings produced are relatively brittle.—ALL. 15083

5.9.4, 6.3.8

**Anodization of Lead and Lead Alloys in Sulfuric Acid.** J. BURBANK. U. S. Naval Research Lab. *J. Electrochem. Soc.,* **104,** No. 12, 693-701 (1957) Dec.

Anodic lead dioxide coatings formed on lead and selected lead alloys (calcium, antimony, tin) in sulfuric acid were examined by electron and x-ray diffraction and by electron and light microscopy. Self-discharge of dioxide films was followed by time-potential curves; relation between anodic attack, self-discharge characteristics and microstructures of metals is reported. Anodically formed dioxide coatings on lead and its alloys comprise mixture of 2 polyorphic forms of lead dioxide at metal-coating interface and common tetragonal lead dioxide at solution-coating interface. $\beta$ lead dioxide discharges more rapidly than $\sigma$ lead oxide. Potential of discharging surface is determined by these relative rates and by physical structures of dioxide layers. Metals are preferentially attacked at grain boundaries and in inter-dentritic areas depending on nature of segregated material and structural discontinuities. Discussion of crystal chemistry of lead compounds, potential-pH diagram and lead acid cell is included. Tables show relation of microstructure to corrosion topography and give typical diffraction patterns of anodic corrosion products. Graphs, photomicrographs.—INCO. 15220

## 6. MATERIALS OF CONSTRUCTION

### 6.2 Ferrous Metals and Alloys

6.2.2, 3.5.8

**Fatigue Properties of Gray Iron.** F. R. BROTZEN AND J. F. WALLACE. Chapter in Gray Iron Castings Handbook (Gray Iron Founder's Soc.) *Machine Design,* **29,** No. 25, 154-158 (1957) Dec. 12.

Fatigue properties of gray or unalloyed irons and low-alloy gray iron (with less than 3% total alloy content) are discussed. Endurance limit and endurance ratio, influence of stress conditions and notch sensitivity are reviewed. Effects of overstressing and understressing; of surface rolling and surface finish; of structure, composition, section size and heat treatment; and of elevated and low temperatures are considered. Tables and graphs show pertinent data.—INCO. 15203

6.2.2

**Alloy Cast Irons Can Solve Tough Problems.** J. H. CULLING AND J. F. WALLACE. Adapted from section of forthcoming Iron Castings Handbook, Gray Iron Founders' Soc., C. F. Walton, editor. *Materials in Design Eng.,* **46,** No. 5, 140-144 (1957) October.

Corrosion resistant irons considered are high-silicon (Duriron, Durichlor), high-chromium and high-nickel irons (Ni-Resist). Heat resistant irons are classified as high-silicon (Silal, Nicrosilal), high-chromium, high-nickel (Ni-Resist and nickel-chromium-silicon iron) and high-aluminum irons. Special purpose irons include low expansion irons (34-36 nickel) and electrical resistance irons. High alloy ductile irons include high-silicon (2.5-6.0), high-nickel (18-22) and still higher-nickel (21-24) types. Table lists physical and mechanical properties of these various types. Graphs show oxidation resistance, creep strength and short time tensile strength at elevated temperatures for the heat-resistant grades.—INCO. 15217

6.2.2, 4.3.2

**Dissolution of Iron in Acidified Chromic Chloride Solution.** ROBERT SKOMOROSKI AND CECIL V. KING. *J. Electrochem. Soc.,* **104,** No. 7, 417-419 (1957) July.

The rate of dissolution of iron from rotating cylinders was studied in 4M hydrochloric acid containing purple and green chromic chloride, also aluminum chloride and sodium chloride up to 0.2M. These salts affect the rate of dissolution somewhat, but chromic ion does not undergo reduction. While the standard potentials predict that reduction is pissoble, the actual potential of iron in acid solutions is not sufficiently negative. Cathodic polarization did not accomplish direct or indirect reduction of chromic ion, but only cathodic protection of the iron. It was also shown that metallic iron catalyzes the oxidation of chromous ion by hydrogen ion. 14985

6.2.2

**The Present State of Development of Iron-Aluminum-Base Alloys.** W. J. LEPKOWSKI AND J. W. HOLLADAY. Battelle Memorial Inst., Titanium Metallurigal Lab., Columbus, Ohio. November 18, 1857, 45 pp.

The purpose of this memorandum is to summarize the present state of development of iron-aluminum-base alloys. The binary iron-aluminum alloys offer favorable tensile strength but possess very poor ductility. The iron-aluminum-molybdenum alloy, thermol (iron-16 aluminum-3 molybdenum), is corrosion resistant, offers excellent tensile strength and is ductile.—NSA. 15356

6.2.2, 3.5.3, 2.3.7

**The Resistance of Cast Iron to Cavitation Erosion.** R. I. HIGGINS. British Cast Iron Research Association. *J. Research and Development,* **7,** No. 2, 28-53 (1957) October.

Tests carried out on jet impact machine and magnetostriction apparatus to assess resistance of various cast irons to cavitation erosion. In jet impact machine, specimens were rotated at high speed through jet of water (fresh and synthetic sea water). Calculated impact pressure was about 7.5 tsi. Effects of carbon, phosphorus and silicon contents; influence of graphite form, of matrix in nodular cast iron and of continuity of matrix; and relationship between impact erosion index and mechanical properties of cast iron are discussed. Attack in jet impact machine is largely mechanical. Within homogeneous series of cast irons the order of merit increases with increase in tensile strength; judged by this test, order of merit depends on strength and continuity of matrix. In magnetostriction apparatus, specimens were vibrated at 10,000 cycles/sec but through very small amplitude. Results from magnetostriction test show that an appreciable amount of corrosion attack occurs, par-

ticularly on unalloyed ferrous materials. Cathodic protection reduces, but does not eliminate, the total attack. There is no simple correlation between results from jet impact machine and particular magnetostriction apparatus used in this investigation. Test apparatus is described and illustrated. Graphs and numerous tables summarize results for various cast irons and nodular irons (1-21.7 nickel) as well as aluminum bronze, manganese bronze, 70-30 brass and mild steel.—INCO 15330

6.2.3, 6.2.5, 8.4.5
**Carbon Steel for High Temperature Reactor Systems.** W. L. PEARL. General Electric Company, Hanford Atomic Products Operation. U. S. Atomic Energy Commission Pubn., HW-33641-(Del.), November 2, 1954 (Declassified with Deletions March 14, 1957), 11 pp. Available from office of Technical Services, Washington, D. C.

An evaluation of the feasibility of utilizing carbon steel as an alternate material for stainless steel in future reactor design is made. Problems and recommendations for future study are noted.—NSA. 15394

## 7. EQUIPMENT

### 7.7 Electrical, Telephone and Radio

7.7, 8.8.3
**Protection of Germanium Rectifiers for Electroplating.** S. P. JACKSON. Gen. Elec. Co. *Products Finishishing,* **21,** No. 5, 36-40 (1957) Feb.

Conditions which may cause corrosion of germanium rectifiers in electroplating plants include air-borne particles, corrosive gases and vapor, condensation, and splashing of plating bath. Rectifier casing serves as major barrier against corrosive gases or liquids. To ensure proper protection, base metal should be phosphatized, and zinc chromate primer and final rubber or vinyl base paint applied.—INCO. 13806

7.7, 3.5.3
**Relay Contact Life in Central Offices.** A. P. GOETZE. *Bell Labs. Record,* **35,** No. 2, 65-68 (1957) Feb.

Discussion of studies of erosion characteristics of various contact metals. When relay contacts open or close to control current in a circuit, there is always some degree of erosion proportional to amount of energy dissipated at contacts. Originally, 2 sizes of contacts, both made entirely of precious metal, were specified. These two sizes of contact were superseded by a bimetal contact consisting of a layer of precious metal superimposed on a nickel base. Bimetal contact has an erosible volume intermediate between former heavy and small contacts. Among factors that affect contact life is length of lead between a contact and its load; with palladium contacts a shorter life is obtained with long leads. Graphs, diagram.—INCO. 13825

### 7.10 Other

7.10, 6.4.2
**Considerations Concerning the Manufacture of Aluminium Cooking Utensils.** (In German.) H. KESSLER. *Aluminum,* **33,** No. 2, 103-106 (1957) Feb.

Based on the chemical analysis and electrochemical testing of an aluminum pressure cooker which, owing to poor materials and faulty workmanship, had failed in service, the basic principles for the manufacturing of aluminum kitchenware are laid down. The alloys used should not contain either zinc or copper, moreover, units which consist of more than one component should be made entirely of the same material. Recommended are the aluminum-magnesium, aluminum-manganese, aluminum-magnesium-manganese alloys, and in special cases aluminum-silicon also. All these, together with pure aluminum, may be used for the production of cast or rolled and deep drawn products. Metallizing of less noble metals with a nobler one, when the resulting deposit is not expected to be pore-free, is strongly discouraged. Similarly, inclusions of carbon particles, which also may originate local currents and, thus, lead to material removal in electronegative metals, should be carefully eliminated.—ALL. 13817

## 8. INDUSTRIES

### 8.3 Group 3

8.3.5, 7.5.2, 5.4.8
**Safety of Inside Enamel Coatings Used in Food Cans.** M. IVES AND G. M. DACK. *Food Research,* **22,** No. 1, 102-109 (1957); *Packaging Absts.,* **14,** No. 5, 383-384 (1957).

Cans with 5 representative coatings used for different classes of foods were tested. A diet designed to evaluate the


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safety of these coatings was fed to rats for 24 months and to monkeys for 12 months. Results showed no adverse effects.—RPI. 14694

8.3.5, 5.3.2, 6.3.14

**The Anaerobic Corrosion of Tin in Anthocyanin Solutions and Fruit Syrups.** F. W. Salt and J. G. N. Thomas. *J. Applied Chem.*, **7**, Pt. 5, 231-238 (1957) May.

Chrysanthemin, main constituent of the coloring matter of Victoria plums and rasberries, acts as a cathodic depolarizer for corrosion of tin by citric and malic acids. About 5 moles of chrysanthemin are required for dissolution of 1 mole of tin but it is probable that this equivalence varies with concentrations of anthocyanin and its tin complex. Rate constants were determined for reaction of tin with a malic acid solution of chrysanthemin and with anaerobic syrup from bottled yellow plums, Victoria plums and raspberries. Amount of tin dissolved per unit volume of syrups increased in order in which they were mentioned and is greater than would be expected from their anthocyanin contents, indicating that other depolarizers are present in the fruit syrups. Graphs, 17 references.—INCO. 14424

8.3.5

**Corrosion in a Corn Milling Plant.** C. H. Pelton. Paper before 8th Plant Maintenance and Eng. Show., Cleveland, 1957. *Ind. and Eng. Chem.*, **49**, No. 5, 65A-66A, 68A, 70A, 74A (1957) May.

Many large-scale corrosion problems are encountered in Clinton corn processing plant which processes corn into bulk food products. Corn is steeped, ground and separated in large volumes of water containing very corrosive sulfur dioxide resulting in process waters containing sulfurous acid. Starch is hydrolyzed to soluble sirups and sugars in presence of hydrochloric acid and at a very low pH and high temperature. After hydrolysis, partially neutralized chloride-containing liquors are handled at near-boiling temperatures and on acid side at a pH of 4.0-5.0. Many of the liquors contain activated carbon which is used as a decolorizing agent; no combination is more corrosive in process. Stainless steels are in general use all over plant. Type 304 is specified in tube applications where proper annealing can be assured for maximum corrosion resistance. Extra low carbon grade of Type 316 is specified for all tanks and large process equipment which cannot be annealed after fabrication. Photos.—INCO. 14335

## 8.4 Group 4

8.4.5, 3.4.8

**In-Reactor Autoclave Corrosion Studies. II. Autoclave Z-18.** K. S. Warren, R. J. Davis, and G. H. Jenks. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-57-3-112, March 22, 1957, 22 pp. Available from Office of Technical Services, Washington, D. C.

In order to test the effect of chromate ion on the corrosion of Zircaloy-2, a 0.04*M* uranyl sulfate solution containing added acid, copper sulfate, and 557 ppm of chromium(VI) was autoclaved with rocking at 280 C for about eight days in the HB-5 facility of the LITR. The average corrosion rate established by the rate of consumption of oxygen was 9.9 mpy at a power density of 4.9 w/ml. It is indicated by comparison with a previous corrosion study under LITR radiation that the presence of chromium(VI) had no significant effect on the radiation corrosion of Zircaloy-2 by enriched uranyl sulfate solutions. However, the data are not conclusive and may be interpreted as showing a low corrosion rate for a limited period (i.e. a short term inhibition) followed by correspondingly rapid corrosion. (auth.)—NSA. 14415

8.4.5, 4.3.2

**Corrosion of Stainless Steels by Nitric Acid-Hydrofluoric Acid-Aluminum Nitrate Mixtures During Evaporation of Plutonium Product Streams.** T. A. Arehart and T. C. Runion. Oak Ridge National Lab. U. S. Atomic Energy Commission Publication, CF-52-11-76, Nov. 10, 1952 (Declassified Feb. 14, 1957), 6 pp. Available from Office of Technical Services, Washington, D. C.

The rate of corrosion of stainless steels during the evaporation of hydrofluoric acid-nitric acid mixtures is quite high even in the presence of excess aluminum. The corrosion rate was six to ten times the rate normally considered permissible.—NSA. 14586

8.4.5, 4.3.3

**Quarterly Report of the Solution Corrosion Group for the Period Ending January 31, 1957.** J. C. Griess, H. C. Savage, J. L. English, R. S. Greeley, S. R. Buxton, D. N. Hess, W. C. Ulrich, T. H. Mauney and E. F. House. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-57-1-144, Jan. 31, 1957, 48 pp. Available from Office of Technical Services, Washington, D. C.

A second test of the mockup of Zircaloy-stainless steel transition joint as used in the HRT reactor vessel was completed. Long-term runs with uranyl sulfate solutions of concentration proposed for use in the HRT have shown the solution stable at 300 C. Experiments with chromic acid for pretreatment of stainless steel have shown that, under certain conditions, the pretreated film can exist in uranyl sulfate in excess of the critical velocity. The practicability of using titanium inserts in highly turbulent areas of stainless steel loops to minimize corrosion was demonstrated. The corrosiveness of beryllium sulfate solutions containing dissolved uranium trioxide was determined at 250 and 280 C. Studies on stress-corrosion cracking of stainless steel in boiling uranyl sulfate containing 25 and 50 ppm $Cl^-$ have shown that it will crack. A number of zirconium-base alloys were prepared and tested in uranyl sulfate for corrosion resistance. (For preceding period see CF-56-10-13.)—NSA. 14603

8.4.5, 3.5.8

**Stress Corrosion in the HRT Mockup.** P. H. Harley. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-57-5-98, May 20, 1957, 20 pp. Available from Office of Technical Services, Washington, D. C.

Stress corrosion was found in 8 components of the HRT mockup; only four of these actually shut down the loop. All of the failures have occurred in the high-pressure system of the loop.—NSA. 14604

8.4.5, 1.6

**Corrosion and Wear Handbook for Water-Cooled Reactors.** D. J. DePaul, Editor. U. S. Atomic Energy Commission. Book, 1957, 293 pp. McGraw Hill, 330 W. 42nd St. New York 36, N. Y.

Background information for engineers and scientists who are encountering for the first time the problems associated with the use of high purity, high temperature water as a reactor coolant. Tabulated data and detailed information for use as reference material for actual design work. Special types of corrosion and application problems involving wear.—BTR. 14659

8.4.5

**Second and Third Operating Test of HRT Core Vessel Transition, Joint and Expansion Bellows Mockup.** R. S. Greeley, W. C. Ulrich, H. C. Savage, J. C. Griess and T. H. Mauney. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-57-4-44, April 30, 1957, 39 pp. Available from Office of Technical Services, Washington, D. C.

Second and third tests were conducted on an expansion bellows and Zircaloy-stainless steel transition joint assembly, duplicating that used in the core-pressure vessel assembly of the HRT. The assembly was exposed for 1140 hours in the second test and 167 hours in the third to a circulation solution containing 0.04*m* uranyl sulfate, 0.02*m* sulfuric acid, and 0.005*m* cupric sulfate in a 100A dynamic corrosion loop under conditions simulating reactor startup, shutdown, and steady-state operation. Results indicated that the transition joint assembly as tested was mechanically sound and leak-tight. Pit-type corrosion continued on the expansion bellows where the upper retaining tangent contacts the bellows. Results are included of specimens exposed to the circulating solution during transition joint and bellows test. —NSA. 14633

8.4.5, 4.3.3

**Corrosion by Aqueous Reactor Fuel Solutions.** H. F. McDuffie. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-56-11-72, Nov. 14, 1956 (Declassified March 12, 1957), 58 pp. Available from Office of Technical Services, Washington, D. C.

A review of experimental work on corrosion of reactor systems by aqueous reactor fuel solutions is presented. Corrosion of titanium, platinum, austenitic stainless steels, zirconium, nickel alloys, and zirconium alloys by uranyl sulfate solutions is discussed.—NSA. 14726

8.4.5

**Use of Hood Cells for Enclosing Low Level Radiation Processes.** Homer A. Moulthrop. General Electric Co., Hanford Atomic Products Operation. U. S. Atomic Energy Comm. Pubn., HW-47022(Rev.), Feb. 28, 1957, 11 pp. Available from Office of Technical Services, Washington, D. C.

The design of hood cells for enclosing low-level radiation processes is discussed. The study includes maintenance, equipment changes, operating costs, corrosion and safety.—NSA. 14716

8.4.5

**Summary of Corrosion Data for HRT Mockup Operational Period Ending November 5, 1956.** R. E. Wacker and J. C. Griess. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-57-5-71, May 22, 1957, 49 pp. Available from Office of Technical Services, Washington, D. C.

The operation of the HRT mockup was on 0.042*m* uranyl sulfate, 0.024*m* sulfuric acid, and 0.005*m* cupric sulfate at 280 C and 1400 psi pressure, with the oxygen content at near 500 ppm. The pump showed bearing wear and high

corrosion. The letdown heat exchanger was removed from the mockup and sectioned. The metallographic examination revealed corrosion. Results of corrosion runs on titanium, Zircaloy-2, and stainless steel are given.—NSA. 14833

8.4.5, 6.6.4

**Surface Studies of Irradiated Graphite.** C. N. SPALARIS. Hanford Atomic Products Operation. U. S. Atomic Energy Comm. Pubn., HW-29082, July 14, 1953 (Declassified Feb. 7, 1957), 28 pp. Available from Office of Technical Services, Washington, D. C.

The effects of oxidation and irradiation on the microsurface structure of pile graphite have been investigated by measuring the surface area and pore size distribution of several samples. The results obtained for both oxidized and irradiated graphite samples indicate that changes in surface characteristics which occur are determined by the flux, temperature of irradiation, and gaseous atmosphere in which the radiation takes place. (auth.)—NSA. 14765

8.4.5, 3.7.3

**Examination of Removable Tube Bundles for Redox.** K. L. SANBORN AND W. R. SMITH. Hanford Atomic Products Operation. U. S. Atomic Energy Comm. Pubn., HW-32642, Sept. 2, 1954 (Changed from Official Use Only Jan. 11, 1957), 28 pp. Available from Office of Technical Services, Washington, D. C.

Metallurgical examination of tube bundles for Redox reveals that the solution heat treatment and quenching operations did not prevent intergranular corrosion. The heat treatment caused distortion. Recommendations which should reduce or prevent these defects are made.—NSA. 14767

8.4.5

**Radiation Damage Studies Program; ETR Loop Materials Progress Report.** M. S. ROBINSON. Phillips Petroleum Co. U. S. Atomic Energy Comm. Pubn., IDO-16337, April 19, 1957, 22 pp. Available from Office of Technical Services, Washington, D. C.

The design of experimental loops for the ETR has required the consideration of some structural metals for which there is little engineering data concerning the change of mechanical properties with neutron irradiation. Samples of the materials have been obtained, and subsize impact and tensile samples are now being irradiated in the MTR. From these samples changes in such properties as tensile strength, hardness, ductility, corrosion resistance and impact strength will be determined. The first group of tensile samples, consisting of: Hastelloy-X, Zircalloy-2, 410 Stainless Steel, 2¼ Croloy, and Inconel-X, has been tested in the MTR hot cell. The 2¼ Croloy, which was nickel plated before reactor insertion, corroded too much to permit further reactor testing. Test data for the other materials and photographs of the samples are presented (auth.)—NSA. 14797

8.4.5

**Summary of Corrosion Data for HRT Mockup Operational Period Ending February 16, 1957.** R. E. WACKER AND J. C. GRIESS. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-57-6-60, June 17, 1957, 41 pp. Available from Office of Technical Services, Washington, D. C.

During the period of operation a total of 576 hours was completed with 1.30*m* uranyl sulfate at 260 C and 1400 psi pressure with the oxygen concentration ~500 ppm. A titanium holder in the suction side of the main circulating line contained coupons of titanium 75A, Zircaloy-2, and types 309 SCb and 347 stainless steel. All coupons contained a heavy, glossy, black paint-like scale. The coupon mounted in the pressurizer heater leg had a rusty film with a trace of yellow precipitate on the bottom of the holder. The corrosion specimen wire mounted in the letdown heat exchanger was removed for examination.—NSA. 14803

8.4.5

**Recovery of Nitric Acid in the Tributyl Phosphate Process for Uranium Recovery. Part 2. (A). Corrosion Studies. (B). Path of Chloride Ion. (C). Path of Tributyl Phosphate.** R. M. WAGNER AND C. GROOT. Hanford Works. U. S. Atomic Energy Comm. Pubn., HW-17937, May 29, 1950 (Declassified Feb. 19, 1957), 12 pp. Available from Office of Technical Services, Washington, D. C.

The corrosion rates for type 316 stainless steel are given for various parts of the distillation system. The path of TBP in distillation of column waste (RAW) and the path of chloride during RAW concentration and nitric acid distillation are outlined.—NSA. 14810

8.4.5, 3.5.4

**Some Aspects of Atomic Energy: The Influence of Radiation on Plant Design.** A. S. WHITE. Paper before Soc. Chem. Industry, Feb. 19, 1957. *Chemistry and Industry*, No. 30, 1020-1027 (1957) July 27.

Discussion of some important aspects in design and operation of nuclear reactors and their associated processing plates. Effects of radiation in uranium, graphite and steel are described. Neutron radiation tends to raise the temperature of the ductile brittle fracture transition of steel as well as to increase yield point and hardness and to reduce ductility. This factor must therefore be added to others, such as welding, corrosion, stress relief, which present problems to the designer of a reactor vessel. Problems in the handling and processing of fissile materials and danger of criticality are discussed. Diagrams, photos, graphs, tables.—INCO. 14815

## 8.5 Group 5

8.5.3

**Combatting Corrosion in a Pulp Mill with Stainless Steel.** J. KOLBERG. Ketchikan Pulp Co. *Chem. Eng. Progress*, **53**, No. 7, 353-356 (1957) July.

Description of corrosion of Type 316 and Hastelloy in Ketchikan Pulp Co. in Alaska caused by fact that chloride level in sulfite acid and recovery system was higher than that of other sulfite mills. Company set up rigid specifications for ordering of new and replacement equipment. For Type 316, most commonly used for sulfite acid service, specifications are 2.75 molybdenum, 0.04-0.06 carbon preferred, with a 0.07 max. Alloy is to be fully annealed. If alloy was cold worked, it must be reannealed followed by a water quench. For fabricated sections all welds are water quenched and if alloy is to be used in an extremely corrosive medium or in a vulnerable location, extra-low carbon alloy is specified. Photos.—INCO. 14669

## 8.8 Group 8

8.8.1, 6.5

**Recent Advances in Metallic Materials of Construction for use in the Chemical Industry.** N. P. INGLIS. Paper, Soc. Chem. Ind. 76th Ann. Meet., London, July 12, 1956. *Chemistry and Industry*, No. 7, 180-189 (1957) Feb. 16.

A review on recent advances in metallic materials of construction for the chemical industry covers corrosion resistent steels, and copper, aluminum, titanium, and their alloys. 11 references. 13790

8.8.1

**Chlorination of Purified Zirconium Oxide.** L. P. TWICHELL. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., Y-574, March 10, 1950 (Declassi-

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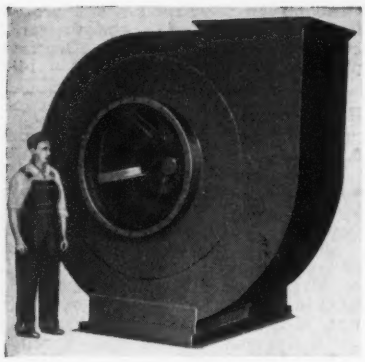

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# INDEX TO ADVERTISERS

Vol. 14 September, 1958 No. 9


| | Page |
|---|---|
| Allen Cathodic Protection Co., Inc. | 127 |
| Amercoat Corporation | Inside Front Cover |
| American Cyanamid Company | 19 |
| Apex Smelting Company | 88 |
| Bakelite Company, Div. Union Carbide Corporation | 11 |
| Bisonite Company, Inc. | 106 |
| Byers, A. M. Company | 99 |
| Carboilne Company | 9 |
| Carpenter Steel Co., Alloy Tube Div. | 110, 111 |
| Cathodic Protection Service | 89 |
| Celanese Corporation of America, Plastics Division | 17 |
| Columbia-Southern Chemical Corp. | 93 |
| Corrosion Engineering Directory | 121 |
| Corrosion Services, Inc. | 94 |
| Day, S. D. Company | 85 |
| Dow Chemical Company | 2, 109 |
| Dowell | 67 |
| Duriron Company | Inside Back Cover |
| Electro Metallurgical Company Division of Union Carbide Corporation | 107 |
| Electro Rust-Proofing Corporation | 80 |
| Erico Products Company | 83 |
| Ervale Corporation | 81 |
| Galloway, The Odis C. Co., Inc. | 5 |
| Good-All Electric Manufacturing Co. | 96 |
| Heil Process Equipment Corporation | 128 |
| Hill, Hubbell and Company, Division of General Paint Corporation | 123 |
| Humble Oil and Refining Company | 16 |
| International Nickel Co., Inc. The | 7 |
| International Paint Company, Inc. | 98 |
| Johns-Manville Corporation Industrial Water Pipe | 1 |
| Underground Pipe Protection | 97 |
| Kraloy Plastic Pipe Company, Inc. | 96 |
| Luzerne Rubber Company, The | 116 |
| May Products, Inc. | 66 |
| Mayes Brothers, Inc. | 104 |
| Minnesota Mining & Manufacturing Company | 101 |
| National Association of Corrosion Engineers | 78, 112, 113 |
| National Carbon Company, Division of Union Carbide Corporation | 91 |
| Perrault Equipment Company | 115 |
| Pittsburgh Coke and Chemical Co. | Back Cover |
| Plastic Products Incorporated | 75 |
| Plastics and Coal Chemicals, Division Allied Chemical Corporation | 130 |
| Positions Wanted and Available | 120 |
| Prufcoat Laboratories, Inc. | 87 |
| Resistoflex Corporation | 18 |
| Rome Cable Corporation | 13 |
| Saran Lined Pipe Company | 103 |
| Smith, Nowery J. | 117 |
| Solvay Process Division Allied Chemical Corporation | 12 |
| Southwestern Plastic Pipe Company | 112 |
| Standard Magnesium Corporation | 14 |
| Tinker & Rasor | 100 |
| Truscon Laboratories, Division of Devoe & Raynolds Co., Inc. | 79 |
| Tube-Kote, Inc. | 71 |
| U. S. Stoneware Company | 15 |
| Universal Oil Products Company | 119 |
| Weaver, Paul E. | 86 |
| Wholesale Coke Company | 81 |
| Wilbur & Williams Company | 74 |
| Williamson, T. D., Inc. | 73 |
| Wisconsin Protective Coating Co. | 108 |
| Wright Chemical Corporation | 125 |
| Yale Sales Company, Yale Machine Works | 129 |

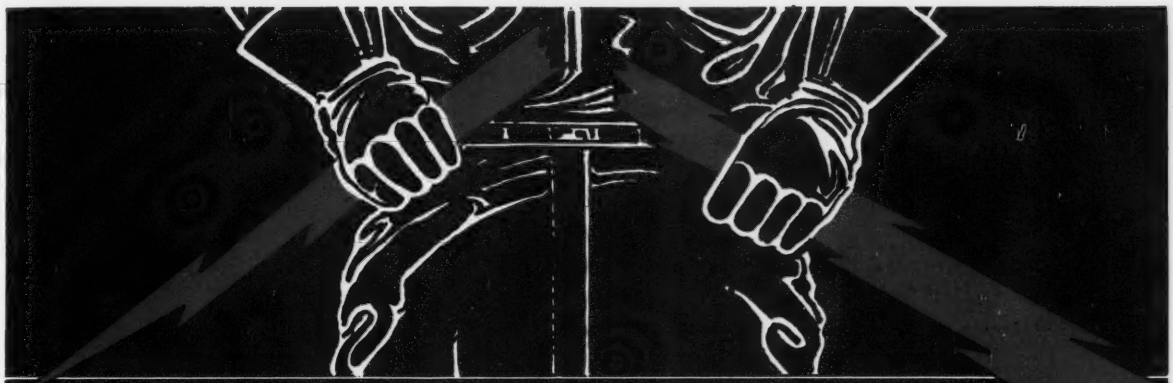

fied Feb. 7, 1957), 17 pp. Available from Office of Technical Services, Washington, D. C.

A series of experiments was made to study various methods of chlorination of zirconium dioxide. Several types of liquid phase reactions were tried without success. Chlorination of the oxide and added carbon by means of chlorine gas at high temperature gave incomplete conversion under the conditions studied. Reaction of oxide with carbon tetrachloride vapor at 500 C gave essentially complete conversion to product of required purity. This was accomplished in a reactor and a condenser both made of nickel to simulate conditions in the large chlorinators available. The reaction was considerably more rapid at 550 to 600 C but the resultant product was highly contaminated with nickel. Studies were also made of the corrosion of nickel and other metals, types of condensers, and degree of ignition necessary in starting oxide. Cost estimates indicate that the oxide could be chlorinated by this method for $0.51 per pound of contained zirconium metal. (auth.)—NSA. 14829

8.8.5

**Racks for Anodizing.** J. E. Bunch. *Metal Finishing*, **55**, No. 7, 45-49 (1957) July.

The use of anodized aluminum as decorative trim by the automotive industry has necessitated the development of satisfactory racks for use during application of the finish to parts. Facts and factors to be considered in designing these racks are considered. These are: 1) basic: processing chemicals generally in use in production installations; metals available for rack construction and their characteristics; elastomers for coating the rack, their characteristics and resistance to chemical reaction at given temperature; 2) primary: equipment and/or machines used to perform the process; the piece to be processed; 3) secondary: holding and positioning of the piece to be processed, mechanical design and construction of the rack; insulation coating, compound formulation and methods of application; initial and maintenance costs, life expectancy, and performance results achieved. Many of the chemicals used are highly corrosive, and become more so with raised operating temperatures, often doubling with each 18 percent rise in temperature. Tables list chemicals used in various processes, the properties of aluminum, copper, phosphorbronze and titanium, which may be used for rack construction, and the physical and chemical characteristics of several materials which may be used for coating anodizing racks.—ALL. 14601



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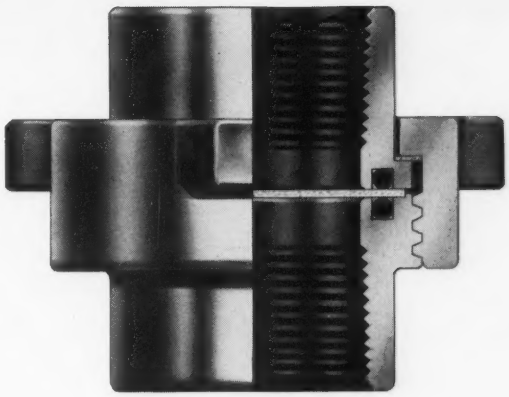

**Figure 110**

## CERTIFIED LABORATORY TESTS PROVE THEIR EFFICIENCY*

RESISTANCE TEST

| Size | Volts Impressed | Resistance at Start—ohms | Resistance at End—ohms | Variation in resistance during time voltage was impressed (1 minute) |
|---|---|---|---|---|
| ¼" | 1,000 D.C. | 11,000,000 | 11,000,000 | None |
| 2" | 1,000 D.C. | 30,000,000 | 30,000,000 | None |

BREAKDOWN TEST

| Size | 60 cycle Breakdown Voltage | Location of Breakdown | Damage to insulating Material |
|---|---|---|---|
| ¼" | 1,500 RMS | Air gap between mating parts | None |
| 2" | 3,500 RMS | Air gap between mating parts | None |

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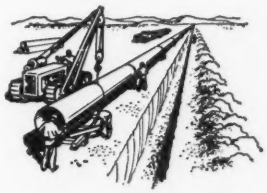
# DURIRON

**ANODE DATA SHEET**

**Number 2 Ground Bed**

*Basic engineering information about* **DURIRON** *impressed current anodes for cathodic protection.*

## Protection of a Pipe Line



**THE PROBLEM:** To protect a pipe line in a creek bed area where coke breeze could not be used due to sandy top soil and quicksand at a four foot depth. The very nature of sandy soil prevents adequate backfilling because it is very prone to caving. The original ground bed of bare scrap iron anodes had a high resistance and showed a tendency to dry out during the year. Adequate protection of the pipe line was not being achieved.

**THE INSTALLATION:** Twenty Duriron Type D Anodes (2" dia. x 60") were installed in two rows, 20 feet apart, with 20 foot spacing in each row as illustrated in Fig. 1. Soil resistivity averaged 2500 ohm-centimeters measured with the four pin method at 10 foot spacing. The anodes were jetted into place using a high velocity stream of water through a 10 foot piece of 1 inch pipe with the top of each anode eventually being approximately three feet below the surface (Fig. 2). Approximately 60 seconds were required to install each anode by this method. The anodes were connected to a 2/0 aluminum header, with the exception of numbers 4, 6, 16, and 17 which were connected to separate number 6 leads and were carried back to the rectifier and connected thereto with 0.01 ohm Holloway shunts. This made possible the reading of individual current values for these four anodes. The connection to the pipe line was by means of an overhead 4/0 copper cable, a distance of about 1000 feet.

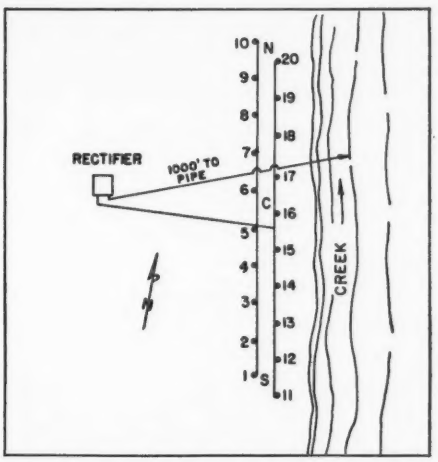
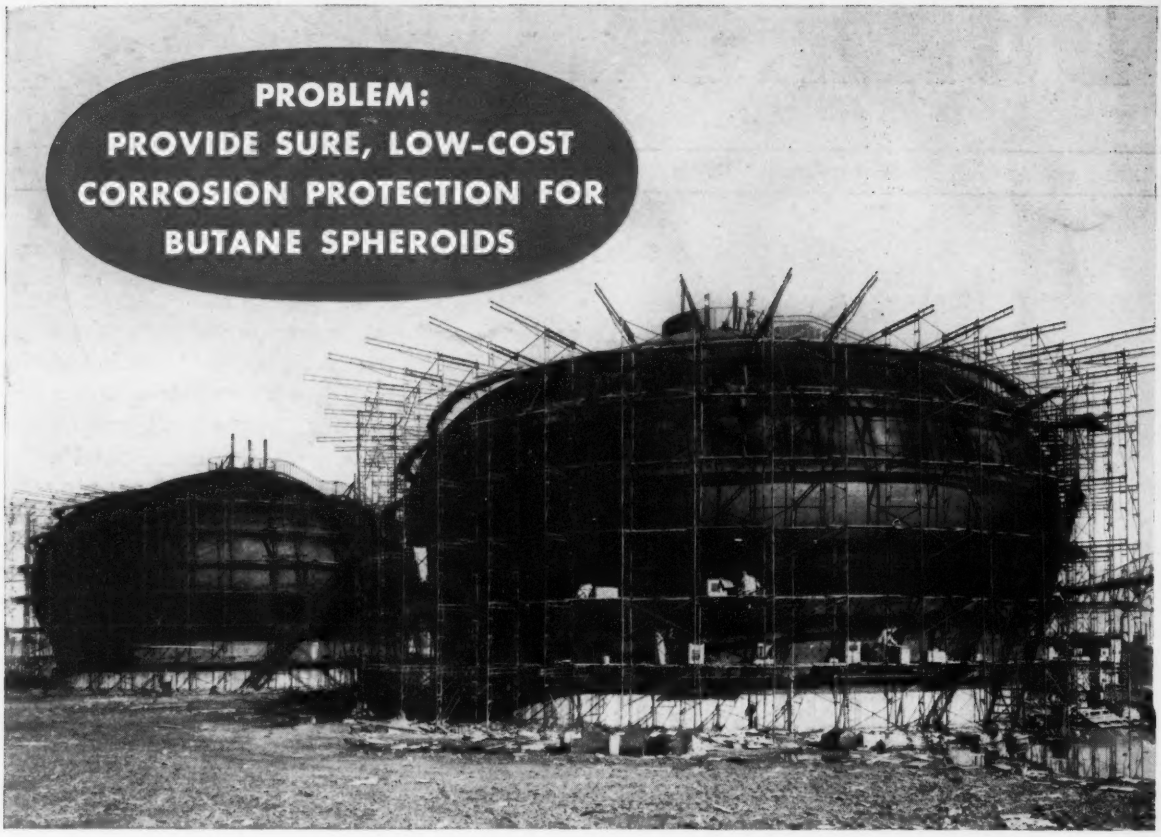



FIG. 1—Illustration of how Duriron Anodes were spaced.

**THE PERFORMANCE TO DATE:** This group of anodes produced 34 amperes (an average of 0.65 amp./sq. ft.) at 46 volts, and after approximately three year's time, these readings have not fluctuated appreciably. Based on initial readings, the resistance of single Type D anodes to ground is approximated by the expression $R=0.005\rho$. (R is the single anode resistance and $\rho$ the soil resistivity in ohm-centimeters.) The loop resistance of sixteen anodes (all except the four with independent leads) was measured as 1.3 ohms; the four, together, read 3.9 ohms; and all twenty indicated 1.2 ohms. This indicates that Duriron anodes can be installed without backfill and operate at appreciable current densities with no noticeable tendency toward gas blocking. The jetting-in process used to install these Duriron anodes was reported to result in considerable savings. It would have been very difficult to install anodes in holes dug by the usual rotary drill method under the ground conditions described above, and it would also have been expensive to transport backfill to this relatively inaccessible locality.

FIG. 2—Illustration of jetting in process.

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